Supplementary Information (SI) for Chemical Communications.

Supporting Information

Nickel-catalyzed Reductive Coupling of Secondary Alkyl Bromides with Alkynes to construct Allylic Difluoromethyl Alkenes

Jinxu Dong[a‡], Xiaohong Wen [a‡], Yihang Xu[a], Jiaming Chen [a], Yanli Yuan [a], Xiaojun Zeng*[ab]

[a] School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi, 330031, China.

[b] Chongqing Research Institute of Nanchang University, Chongqing,402660, China.

[‡] These authors contributed equally.

Table of contents

1. General Information

Unless otherwise noted, all cross-coupling reactions were run under an N_2 atmosphere and all glassware was oven dried before use. Chemicals were purchased from Leyan, (cas 768-60-5, Ethynylanisole, Leyan, Shanghai) Adamas-beta®, Energy Chemical, bidepharm, and Macklin, were used without further purification. DMSO was purchased from Adamas-beta and dried with 4Å molecular sieves. GC/MS analysis was performed on a Thermo-Fischer Scientific ISQ QD single quadrupole mass spectrometer. Thin-layer chromatography (TLC) was performed on 0.20 mm silica gel F-254 plates, with resulting chromatograms visualized by fluorescence quenching or $KMnO_4$ stain. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 297 K on a Bruker AVANCE AV 400 (400 MHz, 101MHz and 376 MHz) spectrometer. Data is reported in ppm using $CDCl_3$ as the solvent unless otherwise specified. Data is reported as: Chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integrated intensity.

2. General Procedure for the Preparation of Substrates

2.1 Commercial Materials

The following known starting materials (alkynes) were commercially available and used without further purification (Figure S1):

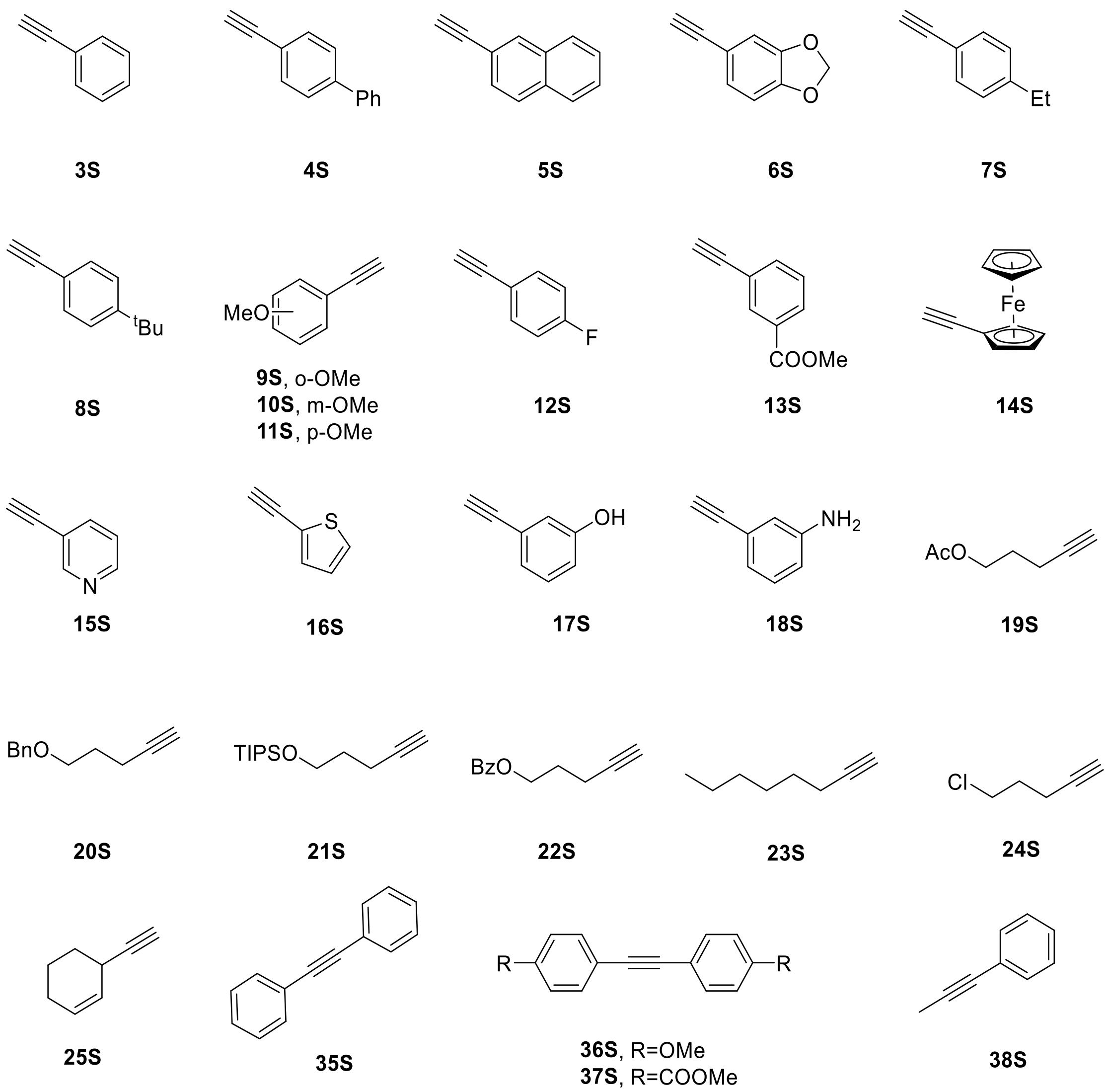


Figure S1. Structural formula of commercially available alkynes

2.2 Prepared Materials

The following known starting materials of Difluoromethyl bromide and Alkynes (Figure S2) were prepared according to the literature procedures: **26S-33S, 39S**[1], **40S**[2], **41S**[3], **42S**[4].

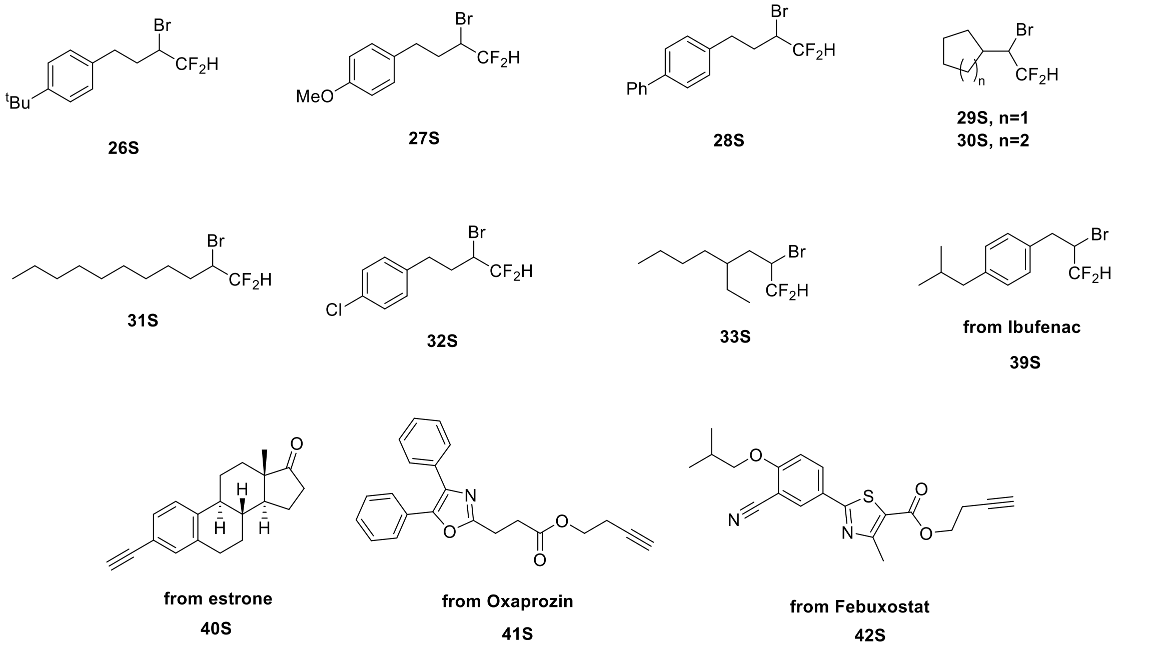
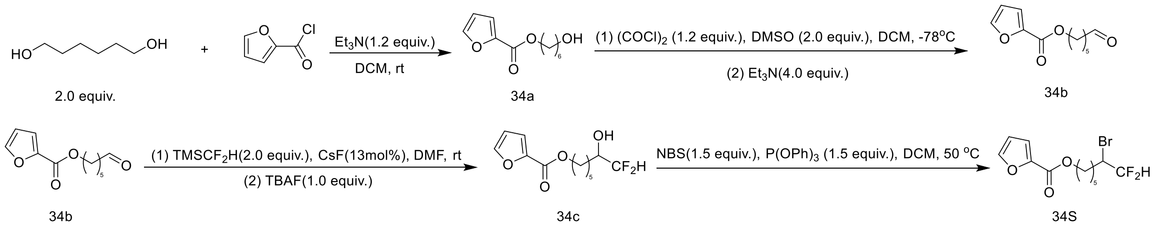


Figure S2. Structural formula of difluoromethyl bromide and alkynes

General procedure of synthesis of substrate 34S.



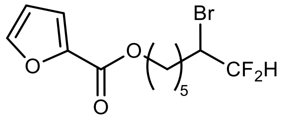
Step 1: In an oven-dried 100 mL round-bottom flask, 1.0 g (8.0 mmol) of 1,6-hexanediol and 16 mL of THF were added, and the mixture was cooled to 0 °C. Triethylamine (1.2 equiv.) was added to the system, followed by the dropwise addition of 520.0 mg (4.0 mmol) of 2-furoyl chloride. The resulting mixture was heated to 50 °C and stirred for 3 hours. The reaction mixture was then diluted with 15 mL of H_2O and extracted with pentane (3 × 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product (**34a**).

Step 2: In an oven-dried 100 mL Schlenk flask, oxalyl chloride (453 mg, 1.2 equiv.) and dichloromethane (10 mL) were added in 1-(furan-2-yl)-6-hydroxyhexan-1-one (**34a**) (3.0 mmol, 1.0 equiv.), and the mixture was cooled to -78 °C. Dimethyl sulfoxide

(6 mmol, 2.0 equiv.) was then added dropwise, and the resulting mixture was stirred for 30 minutes. The alcohol was subsequently added dropwise to the reaction mixture and stirred for 1 h. Triethylamine (1.2 g, 4.0 equiv.) was then introduced, and the reaction was warmed to rt and stirred for 2 h. The reaction mixture was then diluted with 15 mL of H_2O and extracted with pentane (3 × 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product **(34b)**.

Step 3: Under N_2 atmosphere, CsF (47.2 mg, 0.13 equiv.) was added to a solution of 7-(furan-2-yl)-7-oxoheptanal (**34b**) (2.4 mmol, 1.0 equiv.) and Me_3SiCF_2H (1.2 g, 4.8 mmol, 2.0 equiv.) in 4 mL of DMF, then the mixture was stirred at room temperature overnight. A solution of TBAF (2.4 ml, 1 M in THF) was then added, and the whole mixture was stirred for another 1 h. After extraction with Et_2O and H_2O, the organic phase was washed with brine, and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography to get 8,8-difluoro-1-(furan-2-yl)-7-hydroxyoctan-1-one (**34c**).

Step 4: Triphenylphosphite (2.34 g, 4.8 mmol, 1.5 equiv.) and 8,8-difluoro-1-(furan-2-yl)-7-hydroxyoctan-1-one (**34c**) was added over 5 min to a solution of NBS (N-bromosuccinimide) (1.34 g, 7.5 mmol, 1.5 equiv.) in CH_2Cl_2 (15 mL) at 0 ^oC. Next, a solution of the alcohol (5 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added to the mixture at 0 °C. The reaction mixture was heated to 50 ^oC and then stirred for 6 h. Next, the solvent was evaporated, and the product (**34S**) was purified by flash chromatography on silica gel, yield: 23%, 373.6 mg.



34S

7-bromo-8,8-difluoro-1-(furan-2-yl)octan-1-one (**34S**); yellow oil.

$\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 20:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (s, 1H), 7.17 (d, J = 3.5 Hz, 1H), 6.50 (dd, J = 3.6, 1.7 Hz, 1H), 5.83 (td, J = 55.9, 3.8 Hz, 1H), 4.31 (t, J = 6.6 Hz, 2H), 4.07 – 3.74 (m, 1H), 2.07 – 1.94 (m, 1H), 1.86 – 1.75 (m, 3H), 1.72 – 1.66 (m, 1H), 1.59 – 1.40 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.9, 146.4, 144.9, 118.0, 114.9 (t, J = 279.3 Hz), 111.9, 64.8, 50.6 (t, J = 24.0 Hz), 30.8 (t, J = 2.8 Hz), 28.5, 26.6, 25.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.92 – -127.23 (m).

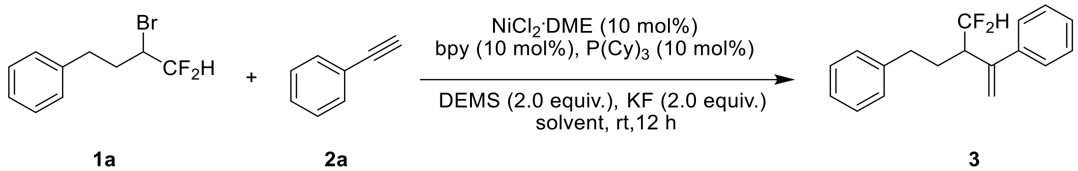
HRMS (ESI) *m/z* calcd for $C_{12}H_{16}BrF_2O_3$[(M+H)$^+$]: 325.0245, found:325.0240.

3. Optimization Studies

3.1 Screening of Reaction Conditions for the Cross-coupling Product

General procedure: In a nitrogen-filled glovebox, to an 8 mL vial equipped with a stir bar was added catalyst (0.01 mmol, 10 mol%), [N] ligand (0.01 mmol, 10 mol%), [P] ligand (0.01 mmol, 10 mol%), base (2.0 equiv.), then [Si-H] (2.0 equiv.) and solvent was added and stirred at rt for 10 min, after that difluoroalkyl bromides **1** (0.1 mmol, 1.0 equiv.) and alkynes (0.15 mmol, 1.5 equiv.) was added to the mixture and stirred for 12 h. After the reaction was completed, the mixture was diluted with EtOAc, the crude product was purified by flash chromatography.

Table S1 The effects of solvent on the reaction $^{a\text{-}b}$.

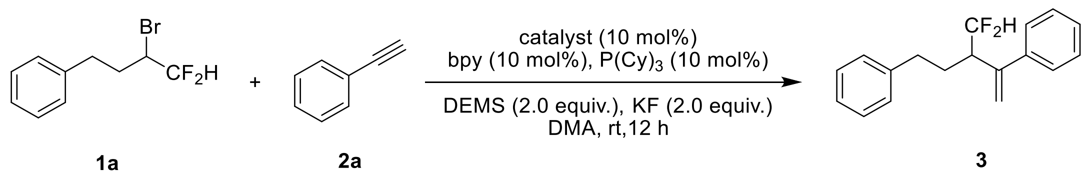


entry	solvent	Yield(%)^b
1	THF	trace
2	DMF	83
3	1,4-dioxane	13
4	MeCN	nd
5	NMP	22

6	DMA	86
7	DMSO	trace

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.), solvent (0.5 mL), rt, 12 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

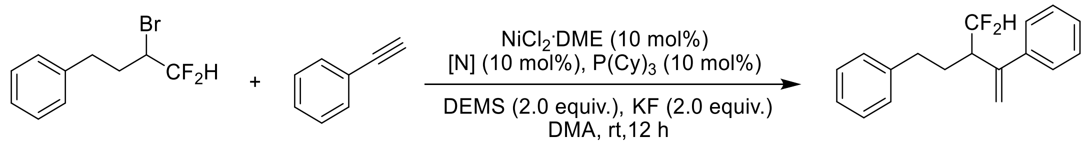
Table S2 The effects of catalysts on the reaction [a-b].



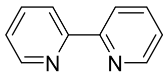
entry	catalyst	Yield(%)[b]
1	$NiCl_2$	37
2	$NiBr_2 \cdot DME$	57
3	$NiCl_2 \cdot 6H_2O$	32
4	$NiBr_2$	40
5	$NiCl_2 \cdot DME$	86
6	$Ni(acac)_2$	nd
7	$Ni(OAc)_2$	11
8	$Ni(OTf)_2$	nd

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.), solvent (0.5 mL), rt, 12 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

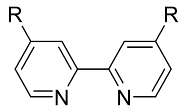
Table S3 The effects of [N] ligand on the reaction[a-b].



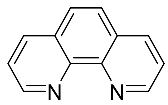
1a **2a** **3**



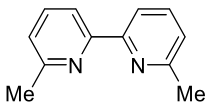
L1



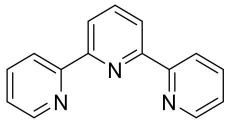
L2, R = OMe
L3, R = COOMe



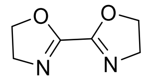
L4



L5



L6

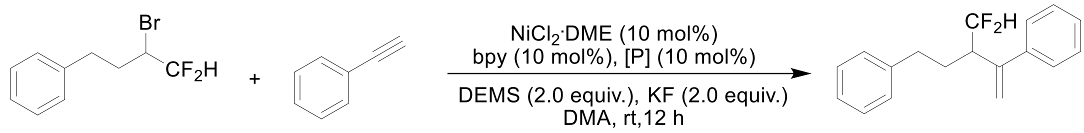


L7

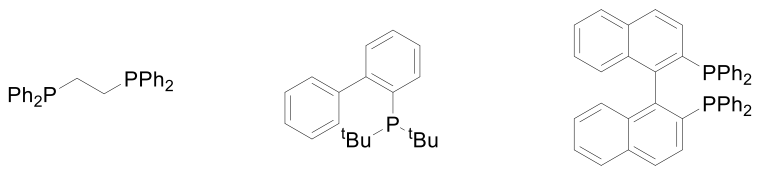
entry	[N] ligand/ $P(Cy)_3$	Yield(%)[b]
1	L1	86
2	L2	74
3	L3	61
4	L4	Trace
5	L5	Trace
6	L6	nd
7	L7	nd

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.), solvent (0.5 mL), rt, 12 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

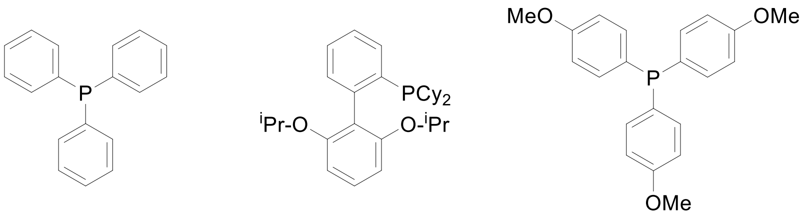
Table S4 The effects of [P] ligand on the reaction[a-b].



1a **2a** **3**



L9 **L10** **L11**

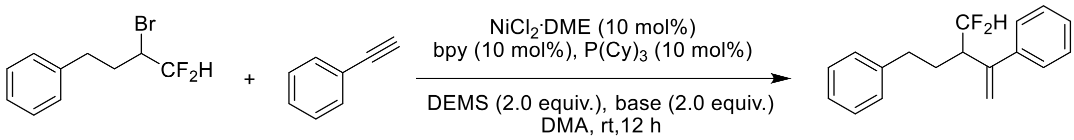


L12 **L13** **L14**

entry	bpy/ [P] ligand	Yield(%)[b]
1	L9	21
2	L10	27
3	L11	51
4	L12	74
5	L13	53
6	L14	67

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.), solvent (0.5 mL), rt, 12 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S5 The effects of base on the reaction[a-b].

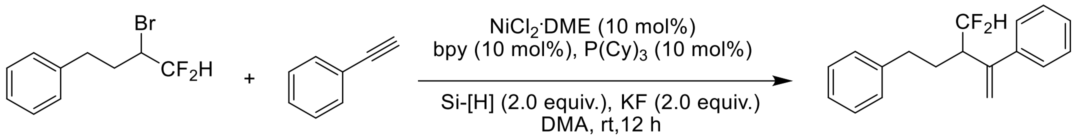


1a **2a** **3**

entry	Base	Yield(%)[b]
1	Cs_2CO_3	14
2	Na_2CO_3	nd
3	K_2CO_3	22
4	KF	86
5	CsF	48
6	K_3PO_4	26
7	$K_3PO_4 \cdot 3H_2O$	nd
8	DABCO	nd

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.), solvent (0.5 mL), rt, 12 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S6 The effects of Si-[H] on the reaction[a-b].



1a **2a** **3**

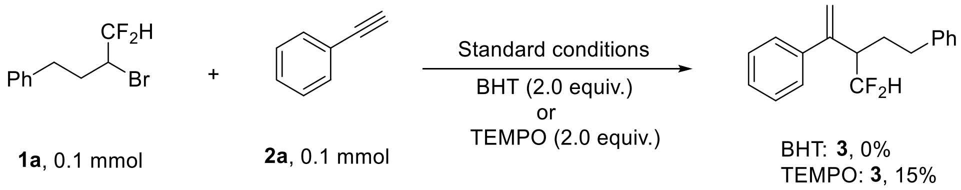
entry[a]	Si-[H]	Yield(%)[b]
1	Et_3SiH	13
2	Ph_3SiH	trace
3	DEMS	86
4	$(MeO)_3SiH$	59

[a] Reaction conditions: secondary alkyl bromides **1a** (0.1 mmol), alkynes **2a** (0.15 mmol), Catalyst (10 mol%), Ligand (10 mol%), [Si-H] (2.0 equiv.), base (2.0 equiv.),

solvent (0.5 mL), rt, 12 h.[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

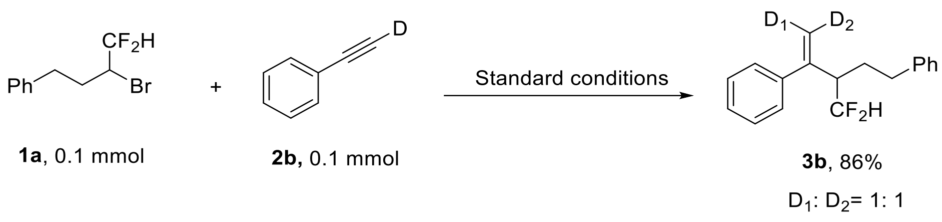
4. Mechanism Studies

4.1 Radical Capture Experiment



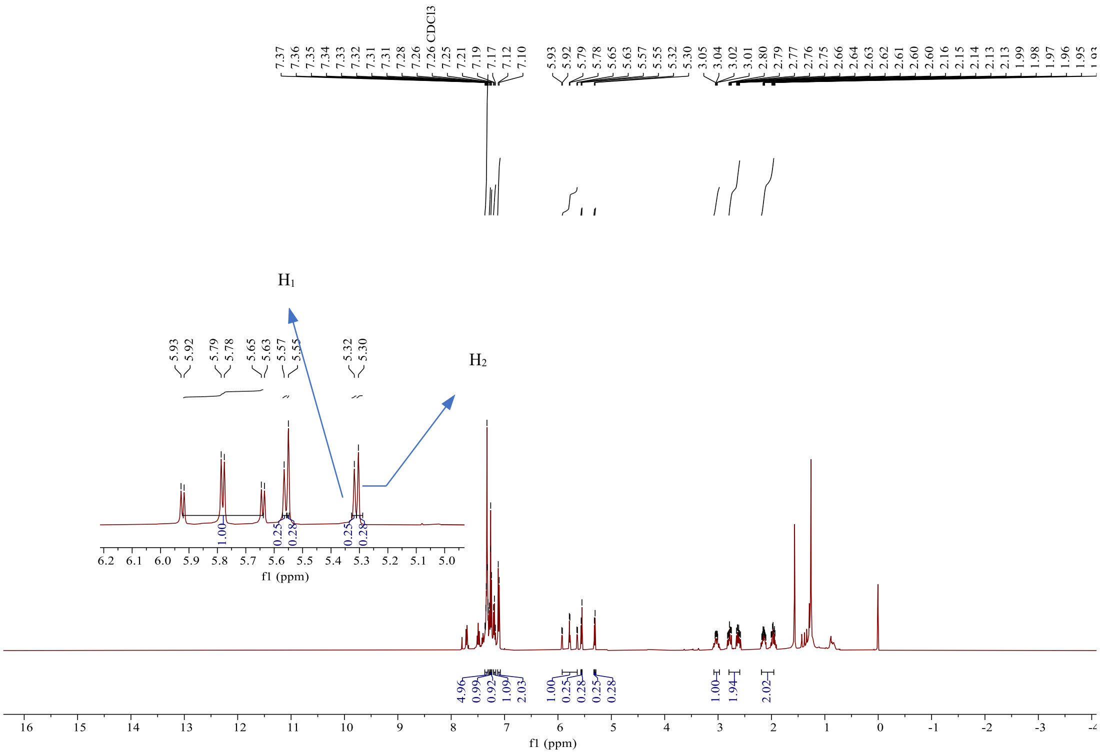
To an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with $NiCl_2 \cdot DME$ (4.4 mg, 0.02 mmol, 10 mol%), and bpy (3.1 mg, 0.02 mmol, 10 mol%), $P(Cy)_3$ (5.6 mg, 0.02 mmol, 10 mol%), KF (23.0 mg, 0.4 mmol, 2.0 equiv.), TEMPO (31.2 mg, 0.2 mmol, 1.0 equiv.) or BHT (44.0 mg, 0.2 mmol, 1.0 equiv.). The tube was sealed with a Teflon-lined screw cap. After evacuated and backfilled with nitrogen three times, alkyne **2a** (0.3 mmol, 1.5 equiv.), DEMS (53.6 mg, 0.4 mmol, 2.0 equiv.) and N, N-dimethylacetamide (0.3 mL) were added via a syringe followed by addition of **1a** (68.1 mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 h under N_2 atmosphere at rt. Then, the mixture was diluted with EtOAc (3 × 10 mL), washed with H_2O and brine. The organic layer was combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography.

4.2 Deuterium-Labeling Experiments

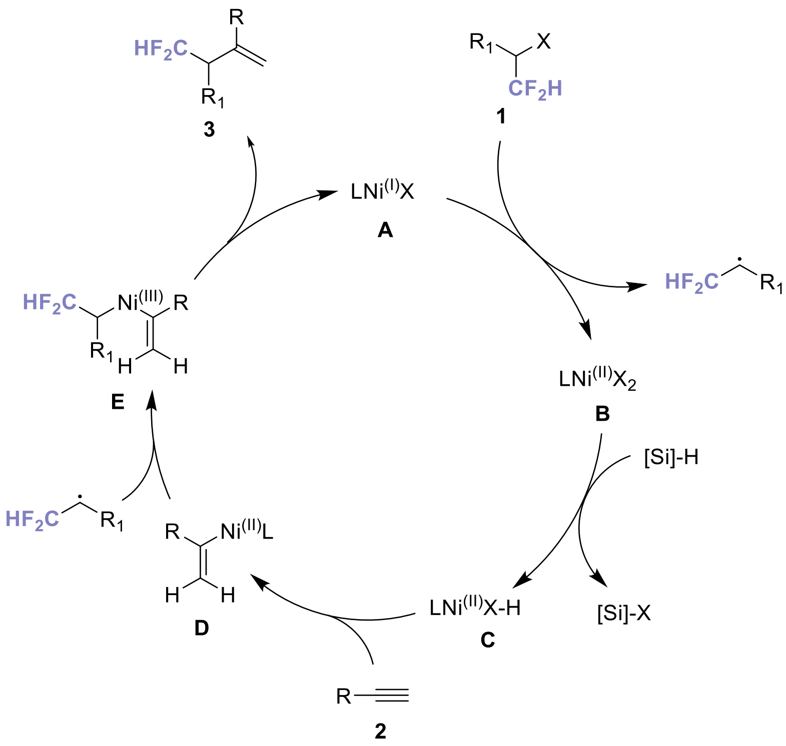


A 5 mL oven-dried screw-cap vial equipped with a magnetic stir bar was charged with $NiCl_2 \cdot DME$ (4.4 mg, 0.02 mmol, 10 mol%), bpy (3.0 mg, 0.02 mmol, 10 mol%), $P(Cy)_3$ (5.5 mg, 0.02 mmol, 10 mol%), and KF (23.0 mg, 0.4 mmol, 2.0 equiv.). The vessel was evacuated and backfilled with N_2. Subsequently, phenylacetylene-D **2b** (0.3 mmol, 1.5 equiv.), difluoromethyl alkyl bromide **2a** (48.0 mg, 0.2 mmol, 1.0 equiv.), DEMS (53.6 mg, 0.4 mmol, 2.0 equiv.), and N, N-dimethylacetamide (0.3 mL) were added via syringe. The reaction was stirred at room temperature for 12 hours.

Upon completion, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a pad of celite. The filtrate was washed with brine (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was analyzed by ^1H NMR spectroscopy. Deuterium incorporation was confirmed by the disappearance or change of the corresponding vinylic proton signal. Quantitative analysis based on the integration of this signal indicated a deuterium incorporation ratio of approximately 1:1.



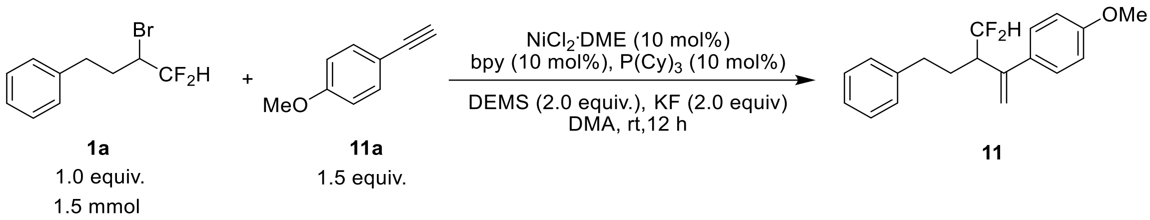
4.3 Proposed Mechanism[5]



5. Synthetic Utility

5.1 Scale Reaction

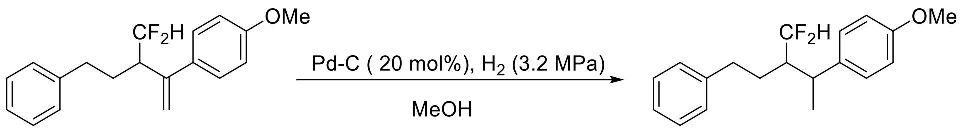
Preparation of difluoroalkylated alkane



$NiCl_2$·DME (33.1 mg, 0.15 mmol, 10 mol%), bpy (23.4 mg, 0.15 mmol, 10 mol%), $P(Cy)_3$ (42.0 mg, 0.15 mmol, 10 mol%) and KF (174.0 mg, 3.0 mmol, 2.0 equiv.) were firstly combined in a 20 mL oven-dried sealing tube. The vessel was evacuated and back filled with N_2 (repeated for 3 times). 1-Ethynyl-4-methoxybenzene **11a** (297.4 mg, 2.25 mmol, 1.5 equiv.), difluoroalkyl bromide **1a** (372.6 mg, 1.5 mmol, 1.0 equiv.), DEMS (301.2 mg, 3.0 mmol, 2.0 equiv.) and N, N-Dimethylacetamide (6 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at 23 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with ethyl acetate (3 × 15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give coupling product **11** in 71% yield (286 mg).

5.2 Synthesis of Diverse Difluoroalkylated Analogues

Preparation of difluoromethylated alkane

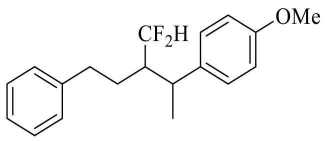


11

43, 95%, dr = 1: 1

In a 25 mL high-pressure reaction vessel, compound **11** (60.2 mg, 0.2 mmol, 1.0 equiv.) and Pd/C (11 mg, 20 mol%) were added. The reaction system was evacuated and purged with hydrogen gas to an internal pressure of 3.2 MPa. The mixture was stirred at room temperature for 16 hours. Upon completion, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a pad of celite. The filtrate was washed with brine (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired product.

Figure 4: Device diagram of product 43



43

1-(3-(difluoromethyl)-5-phenylpentan-2-yl)-4-methoxybenzene (**43**) (57.6 mg, 95%, dr = 1:1); colorless liquid.

R$_f$ =0.7 (petroleum ether)

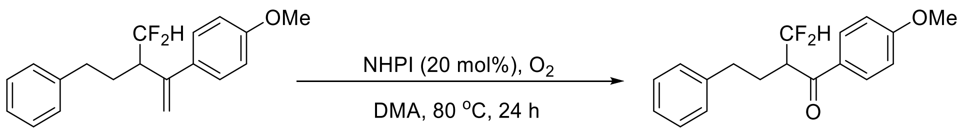
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, *J* = 7.1 Hz, 2H), 7.26 – 7.16 (m, 4H), 7.17 – 7.04 (m, 8H), 6.89 – 6.81 (m, 4H), 5.82 (td, *J* = 51.7, 4.0 Hz, 1H), 5.55 (td, *J* = 52.0, 4.0 Hz, 1H), 3.81 (d, *J* = 1.1 Hz, 6H), 3.06 – 2.86 (m, 2H), 2.82 – 2.46 (m, 4H), 2.06 – 1.85 (m, 3H), 1.81 – 1.66 (m, 3H), 1.31 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.3, 158.3, 142.2, 141.9, 136.3, 136.3, 128.7, 128.6, 128.5, 128.5, 128.5, 126.0, 126.0, 118.9 (t, *J* = 243.4 Hz), 118.7 (t, *J* = 243.4 Hz), 114.1, 114.0, 55.4, 47.9 (t, *J* = 17.8 Hz), 47.3 (t, *J* = 17.8 Hz), 38.2 (d, *J* = 2.5 Hz), 38.2 (d, *J* = 3.0 Hz), 38.0 (d, *J* = 3.1 Hz), 38.0 (d, *J* = 3.4 Hz), 34.3, 34.0, 27.4 (t, *J* = 3.5 Hz), 26.7 (t, *J* = 3.6 Hz), 18.5, 18.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.16 – -120.34 (m), -120.13 – -130.49 (m).

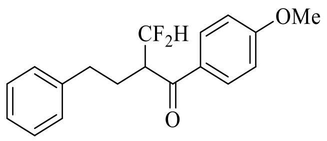
HRMS (EI) *m/z* calcd for $C_{19}H_{22}F_2O$[M$^+$]: 304.1639, found: 304.1636.

Preparation of α-Difluoromethyl Ketone



11 **44**, 57%

In an oven-dried 25 mL sealed tube, N-hydroxyphthalimide (20 mol%) and compound **11** (60.2 mg, 0.2 mmol, 1.0 equiv.) were added. The system was then evacuated and charged with an O_2 filled balloon. The reaction mixture was heated to 80 ℃ and stirred for 24 hours. After cooling, the crude mixture was directly adsorbed onto silica gel and purified by flash chromatography on silica gel using ethyl acetate (20 mL) as the eluent to afford the desired product **44**.



44

2-(difluoromethyl)-1-(4-methoxyphenyl)-4-phenylbutan-1-one (**44**) (34.6 mg, 57%); yellow liquid.

R$_f$ =0.7 (petroleum ether)

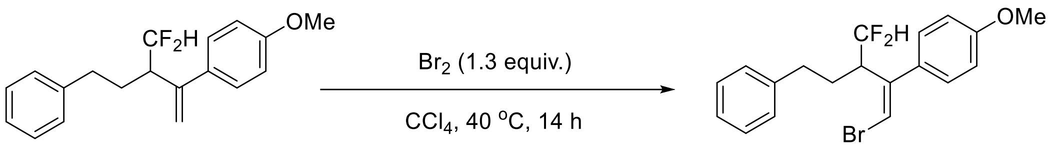
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (dd, *J* = 8.8, 1.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.25 (s, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.04 (td, *J* = 56.2, 6.7 Hz, 1H), 3.88 (s, 3H), 3.91 – 3.80 (m, 1H), 2.73 – 2.53 (m, 2H), 2.28 – 2.14 (m, 1H), 2.13 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.6, 164.2, 140.5, 131.0, 129.7, 128.6, 128.5, 126.3, 117.7 (t, *J* = 243.4 Hz), 114.0, 55.6, 48.9 (t, *J* = 20.3 Hz), 32.8, 29.3 (dd, *J* = 6.0, 2.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -110.33 – -131.06 (m).

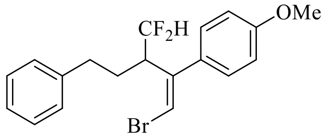
HRMS (EI) *m/z* calcd for $C_{18}H_{18}F_2O_2$[M$^+$]: 304.1275, found: 304.1271.

Preparation of (E)-1-(1-bromo-3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-methoxybenzene



In a 25 mL Schlenk flask, compound **11** (60.2 mg, 0.2 mmol, 1.0 equiv.) was dissolved in carbon tetrachloride. Liquid bromine (0.2 mmol, 2.0 equiv.) was then added to the mixture. The reaction mixture was stirred at 40 °C for 18 hours. Upon completion, the reaction was quenched with a saturated aqueous solution of sodium thiosulfate and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **45**.

2D NMR analysis of the product confirmed the presence of a single configurational isomer.



45

(E)-1-(1-bromo-3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-methoxybenzene (**45**) (49.3 mg, 65%); yellow oil.

R$_f$ =0.6 (petroleum ether)

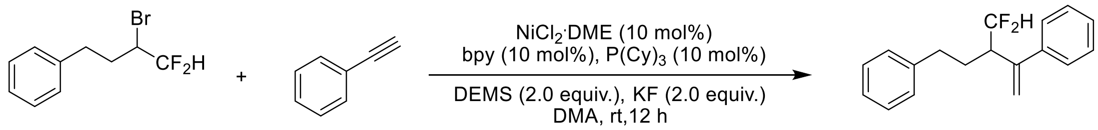
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, *J* = 7.0 Hz, 2H), 7.25 (s, 1H), 7.17 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 5.84 (td, *J* = 56.4, 5.7 Hz, 1H), 3.82 (s, 3H), 3.58 (dt, *J* = 11.0, 5.4 Hz, 1H), 2.79 – 2.56 (m, 2H), 2.06 – 1.97 (m, 1H), 1.91 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.7, 141.4, 131.0, 129.7, 128.6, 128.5, 126.2, 117.03 (t, *J* = 244.1 Hz), 114.0, 110.5, 55.5, 47.8 (t, *J* = 21.1 Hz), 33.2, 29.8, 28.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -105.08 – -133.33 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{19}BrF_2O$ [M^+]: 380.0587, found: 381.0620.

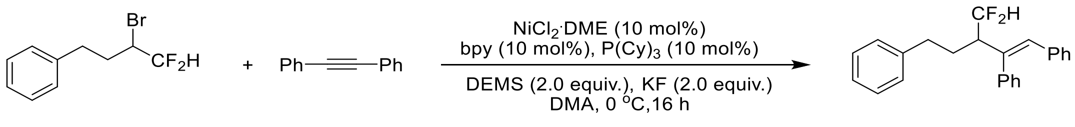
6. General Procedure for the Synthesis of the Product



1a **2a** **3**

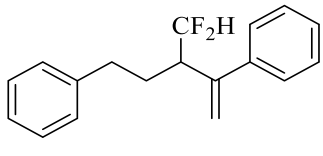
Procedure A: Product **3** as an example: to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with $NiCl_2$·DME (4.4 mg, 0.02 mmol, 10 mol%), and bipyridyl (3.1 mg, 0.02 mmol, 10 mol%), P(Cy)$_3$ (5.6 mg, 0.02 mmol, 10 mol%), KF (23.1 mg, 0.4 mmol, 2.0 equiv.), The tube was sealed with a Teflon-lined screw cap. After evacuated and backfilled with nitrogen three times, alkyne **2a** (0.3 mmol, 1.5 equiv.), DEMS (53.6 mg, 0.4 mmol, 2.0 equiv.) and N, N-Dimethylacetamide (0.3 mL) were added via a syringe followed by addition of **1a** (68.1

mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 h under N_2 atmosphere at rt. After the reaction was completed, the mixture was diluted with EtOAc (3 × 10 mL), washed with H_2O and brine. The organic layer was combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography.



Procedure B: Product **35** as an example: to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with $NiCl_2$·DME (4.4 mg, 0.02 mmol, 10 mol%), and bpy (3.1 mg, 0.02 mmol, 10 mol%), $P(Cy)_3$ (5.6 mg, 0.02 mmol, 10 mol%), KF (23.0 mg, 0.4 mmol, 2.0 equiv.), The tube was sealed with a Teflon-lined screw cap. After evacuated and backfilled with nitrogen three times, alkyne **35S** (0.3 mmol, 1.5 equiv.), DEMS (53.6 mg, 0.4 mmol, 2.0 equiv.) and N, N-Dimethylacetamide (0.3 mL) were added via a syringe followed by addition of **1a** (68.1 mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 h under N_2 atmosphere at 0 ^{o}C. After the reaction was completed, the mixture was diluted with EtOAc (3 × 10 mL), washed with H_2O and brine. The organic layer was combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography.

7. Characterization of Products



3

(3-(difluoromethyl)pent-4-ene-1,4-diyl)dibenzene (**3**) (44.0 mg, 81%); colorless liquid.

R_f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v)

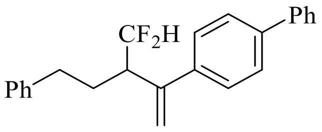
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.34 (m, 1H), 7.33 (d, *J* = 1.6 Hz, 3H), 7.32 (d,

J = 1.9 Hz, 1H), 7.27 (d, J = 6.9 Hz, 1H), 7.25 (d, J = 1.6 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 5.78 (td, J = 56.6, 4.4 Hz, 1H), 5.57 (s, 1H), 5.32 (s, 1H), 3.10 – 2.95 (m, 1H), 2.83 – 2.75 (m, 1H), 2.66 – 2.54 (m, 1H), 2.20 – 2.08 (m, 1H), 2.02 – 1.89 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.4 (t, J = 4.3 Hz), 142.1, 141.4, 128.5, 128.5, 127.8, 126.6, 126.1, 117.9 (t, J = 244.9 Hz), 116.3, 47.5 (t, J = 19.9 Hz), 32.9, 30.0 (t, J = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.89 – -123.41 (m).

HRMS (ESI) *m/z* calcd for $C_{18}H_{18}F_2$ [M$^+$]: 272.1371, found:272.1368.



4

4-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-1,1'-biphenyl (**4**) (53.0 mg, 76%); white soild.

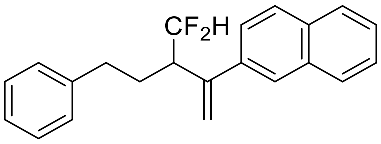
R$_f$ =0.4 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.57 (m, 4H), 7.47 (t, J = 7.7 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.29 (d, J = 6.9 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.15 – 7.12 (m, 2H), 5.82 (td, J = 56.6, 4.4 Hz, 1H), 5.65 (s, 1H), 5.35 (s, 1H), 3.09 (dd, J = 9.9, 3.9 Hz, 1H), 2.81 (td, J = 9.5, 4.9 Hz, 1H), 2.72 – 2.63 (m, 1H), δ 2.25 – 2.14 (m, 1H), 2.07 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0 (t, J = 4.3 Hz), 141.5, 141.1, 140.8, 140.7, 129.0, 128.6, 127.6, 127.3, 127.2, 127.1, 126.2, 118.0 (t, J = 244.3 Hz), 116.3, 47.5 (t, J = 19.8 Hz), 33.0, 30.2 (t, J = 3.9 Hz), 29.9.

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.36 – -126.80 (m).

HRMS (EI) *m/z* calcd for $C_{24}H_{22}F_2$[M$^+$]: 348.1684, found:348.1680.



5

2-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)naphthalene (**5**) (54.3 mg, 84%); white soild.

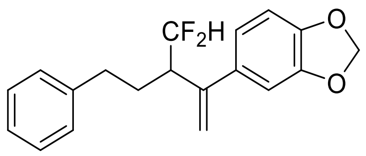
R_f =0.4 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 3H), 7.72 (s, 1H), 7.55 – 7.44 (m, 3H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.14 (d, *J* = 6.9 Hz, 2H), 5.85 (td, *J* = 56.6, 4.3 Hz, 1H), 5.72 (s, 1H), 5.43 (s, 1H), 3.29 – 3.11 (m, 1H), 2.93 – 2.78 (m, 1H), 2.74 – 2.62 (m, 1H), 2.30 – 2.13 (m, 1H), 2.09 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4 (t, *J* = 4.3 Hz), 141.4, 139.4, 133.4, 133.0, 128.6, 128.6, 128.3, 128.3, 127.7, 126.5, 126.3, 126.2, 125.4, 125.0, 118.1 (t, *J* = 245.4 Hz), 116.8, 47.4 (t, *J* = 19.8 Hz), 33.0, 30.1 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.61 – -123.60 (m).

HRMS (EI) *m/z* calcd for $C_{22}H_{20}F_2[M^+]$: 322.1528, found:322.1524.



6

5-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)benzo[d][1,3]dioxole (**6**) (52.2 mg, 83%); colorless liquid.

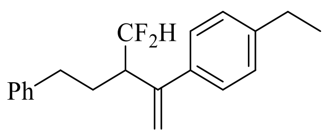
R_f =0.3 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 6.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 6.9 Hz, 2H), 6.85 – 6.76 (m, 3H), 5.98 (s, 2H), 5.77 (td, *J* = 56.6, 4.5 Hz, 1H), 5.49 (s, 1H), 5.24 (s, 1H), 3.03 – 2.89 (m, 1H), 2.82 – 2.70 (m, 1H), 2.68 – 2.55 (m, 1H), 2.25 – 2.09 (m, 1H), 2.01 – 1.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.4, 145.0 (t, *J* = 4.3 Hz), 141.5, 136.5, 128.6, 128.6, 126.2, 120.2, 118.0 (t, *J* = 244.9 Hz), 115.5, 108.3, 107.3, 101.3, 47.8 (t, *J* = 19.8 Hz), 32.9, 30.1 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.95 – -124.57 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{18}F_2O_2[M^+]$: 316.1275, found: 316.1270.



7

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-ethylbenzene (**7**) (38.2 mg, 64%); colorless liquid.

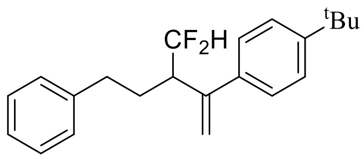
R_f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.2 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.23 – 7.14 (m, 3H), 7.11 (d, *J* = 6.9 Hz, 2H), 5.77 (td, *J* = 56.6, 4.4 Hz, 1H), 5.54 (s, 1H), 5.27 (s, 1H), 3.10 – 2.94 (m, 1H), 2.83 – 2.70 (m, 1H), 2.69 – 2.56 (m, 3H), 2.20 – 2.09 (m, 1H), 2.02 – 1.85 (m, 1H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (t, *J* = 4.4 Hz), 144.1, 141.6, 139.5, 128.6, 128.6, 128.1, 126.6, 126.2, 118.0 (t, *J* = 244.5 Hz), 115.7, 47.6 (t, *J* = 19.8 Hz), 33.0, 30.1 (t, *J* = 4.0 Hz), 28.6, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.25 – -132.61 (m).

HRMS (EI) *m/z* calcd for $C_{20}H_{22}F_2[M^+]$: 300.1684, found:300.1680.



8

1-(tert-butyl)-4-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)benzene (**8**) (50.0 mg, 76%); white soild.

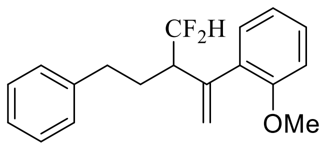
R_f =0.6 (petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.29 – 7.26 (m, 3H), 7.25 (s, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 5.78 (td, *J* = 56.6, 4.3 Hz, 1H), 5.57 (s, 1H), 5.28 (s, 1H), 3.12 – 2.94 (m, 1H), 2.87 – 2.70 (m, 1H), 2.69 – 2.51 (m, 1H), 2.26 – 2.10 (m, 1H), 2.04 – 1.81 (m, 1H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 150.8, 145.1 (t, *J* = 4.3 Hz), 141.5, 139.0, 128.5, 128.4, 126.2, 126.0, 125.4, 117.9 (t, *J* = 245.4 Hz), 115.6, 47.4 (t, *J* = 19.7 Hz), 34.6, 32.9, 31.3, 29.9 (t, *J* = 3.9 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.64 – -123.67 (m).

HRMS (EI) *m/z* calcd for $C_{22}H_{26}F_2$[(M+H)$^+$]: 328.1997, found:328.1992.



9

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-2-methoxybenzene (**9**) (36.1 mg, 61%); colorless liquid.

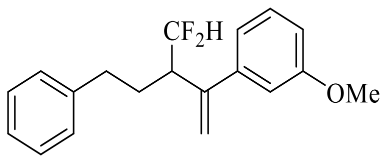
R$_f$ =0.5 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$)δ 7.34 – 7.25 (m, 2H), 7.24 (s, 1H), 7.20 – 7.16 (m, 2H), 7.13 (d, *J* = 6.9 Hz, 2H), 6.95 (td, *J* = 7.4, 1.1 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.89 (td, *J* = 57.0, 3.1 Hz, 1H), 5.41 (s, 1H), 5.35 (s, 1H), 3.76 (s, 3H), 3.12 – 2.92 (m, 1H), 2.85 – 2.76 (m, 1H), 2.69 – 2.58 (m, 1H), 2.20 – 2.06 (m, 1H), 2.04 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 156.5, 145.4 (dd, *J* = 7.7, 2.4 Hz), 142.2, 132.2, 130.5, 129.2, 128.5, 128.5, 126.0, 120.9, 118.0, 117.9 (t, *J* = 244.4 Hz), 110.7, 55.3, 47.7 (t, *J* = 19.7 Hz), 33.3, 29.4 (dd, *J* = 5.1, 2.7 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -106.35 – -135.96 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{20}F_2O$[M$^+$]: 302.1482, found: 302.1478.



10

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-3-methoxybenzene (**10**) (45.1 mg, 75%); colorless liquid.

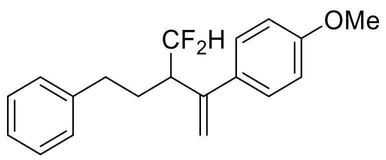
R$_f$ =0.3 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, *J* = 4.9 Hz, 2H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 5.1 Hz, 2H), 5.77 (td, *J* = 56.5, 4.3 Hz, 1H), 5.56 (s, 1H), 5.31 (s, 1H), 3.81 (s, 3H), 3.09 – 2.92 (m, 1H), 2.88 – 2.73 (m, 1H), 2.67 – 2.59 (m, 1H), 2.19 – 2.09 (m, 1H), 2.04 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.7, 145.4 (t, *J* = 4.1 Hz), 143.7, 141.5, 129.6, 128.6, 128.6, 126.2, 119.2, 117.9 (t, *J* = 244.4 Hz), 116.6, 113.2, 112.6, 55.4, 47.7 (t, *J* = 19.9 Hz), 33.0, 30.0 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.48 – -124.15 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{20}F_2O[M^+]$: 302.1482, found: 302.1478.



11

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-methoxybenzene (**11**) (46.1 mg, 77%); colorless liquid.

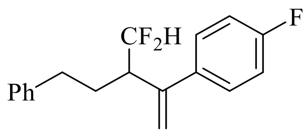
R$_f$ =0.3 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.25 (m, 2H), 7.26 (s, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 6.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.77 (td, *J* = 56.6, 4.5 Hz, 1H), 5.51 (s, 1H), 5.24 (s, 1H), 3.83 (s, 3H), 3.11 – 2.90 (m, 1H), 2.84 – 2.71 (m, 1H), 2.69 – 2.52 (m, 1H), 2.23 – 2.06 (m, 1H), 2.00 – 1.88 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.5, 144.8 (t, *J* = 4.4 Hz), 141.6, 134.6, 128.6, 128.6, 127.8, 126.2, 118.1 (t, *J* = 244.9 Hz), 114.9, 113.9, 55.4, 47.6 (t, *J* = 19.8 Hz), 33.0, 30.1 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.42 – -124.78 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{20}F_2O[M^+]$: 302.1482, found: 302.1478.



12

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-fluorobenzene (**12**) (39.6 mg, 69%); colorless liquid.

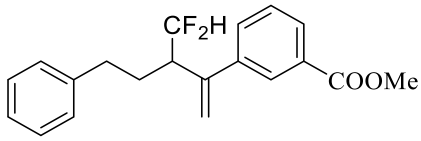
R$_f$ =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 – 7.60 (m, 1H), 7.31 – 7.25 (m, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.07 – 6.96 (m, 2H), 5.76 (td, *J* = 56.6, 4.5 Hz, 1H), 5.52 (s, 1H), 5.30 (s, 1H), 3.07 – 2.87 (m, 1H), 2.82 – 2.69 (m, 1H), 2.66 – 2.53 (m, 1H), 2.19 – 2.07 (m, 1H), 2.00 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 163.8, 161.4, 144.6 (t, *J* = 4.2 Hz), 141.3, 128.6 (d, *J* = 5.9 Hz), 128.4 (d, *J* = 7.9 Hz), 126.3, 118.0 (t, *J* = 244.2 Hz), 116.5, 115.6, 115.4, 47.7 (t, *J* = 19.9 Hz), 32.9, 30.2 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -114.48 – -115.30 (m), -117.35 – -123.06 (m).

HRMS (EI) *m/z* calcd for $C_{18}H_{17}F_3$[M$^+$]: 290.1227, found: 290.1221.



13

methyl 4-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)benzoate (**13**) (27.6 mg, 42%); colorless liquid.

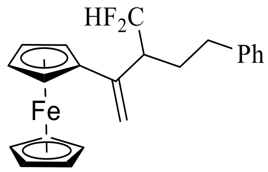
R$_f$ =0.5 (petroleum ether: ethyl acetate, 30:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 – 7.95 (m, 1H), 7.49 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 1.3 Hz, 2H), 7.24 (d, *J* = 1.4 Hz, 2H), 7.23 – 7.15 (m, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 5.78 (td, *J* = 56.4, 4.4 Hz, 1H), 5.62 (s, 1H), 5.38 (s, 1H), 3.93 (s, 3H), 3.14 – 2.95 (m, 1H), 2.82 – 2.72 (m, 1H), 2.66 – 2.54 (m, 1H), 2.25 – 2.10 (m, 1H), 2.02 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 144.7 (t, *J* = 4.3 Hz), 142.6, 141.3, 131.2, 130.6, 129.0, 128.8, 128.6, 128.5, 127.8, 126.3, 117.9 (t, *J* = 245.4 Hz), 117.5, 52.4, 47.6 (t, *J* = 20.2 Hz), 32.9, 30.2 (t, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -109.90 – -137.52 (m).

HRMS (EI) *m/z* calcd for $C_{20}H_{20}F_2O_2$[M$^+$]: 330.1426, found: 330.1423.



14

Ferrocene, (3-(difluoromethyl)-5-phenylpent-1-en-2-yl) (**14**) (54.7 mg, 72%); darkness red solid.

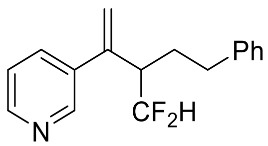
R$_f$ =0.3 (petroleum ether, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 - 7.18 (m, 3H), 5.92 (td, *J* = 56.7, 4.1 Hz, 1H), 5.56 (s, 1H), 5.13 (s, 1H), 4.36 (s, 1H), 4.30 – 4.23 (m, 3H), 4.10 (s, 5H), 2.96 – 2.83 (m, 1H), 2.81 – 2.65 (m, 2H), 2.27 – 2.11 (m, 1H), 2.01 – 1.85 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.6 (t, *J* = 3.9 Hz), 141.6, 128.5, 126.1, 118.1 (t, *J* = 244.7 Hz), 111.4, 86.2, 69.3, 68.9, 68.9, 66.2, 66.1, 46.6 (t, *J* = 19.8 Hz), 33.4, 30.5 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -113.93 – -125.30 (m).

HRMS (EI) *m/z* calcd for $C_{22}H_{22}F_2Fe$[M$^+$]: 380.1034, found:380.1031.



15

3-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)pyridine (**15**) (27.1 mg, 51%); yellow oil.

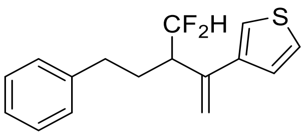
R$_f$ =0.4 (petroleum ether: ethyl acetate, 100:1, v/v)

¹H NMR (400 MHz, CDCl₃) δ 8.69 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 7.12 – 7.08 (m, 2H), 5.78 (td, J = 56.4, 4.5 Hz, 1H), 5.62 (s, 1H), 5.43 (s, 1H), 3.05 – 2.91 (m, 1H), 2.96 – 2.83 (m, 1H), 2.81 – 2.65 (m, 1H), 2.27 – 2.11 (m, 1H), 2.01 – 1.85 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 142.5, 140.9, 134.0, 128.7, 128.5, 126.4, 118.6, 117.8 (t, J = 244.6 Hz), 47.5 (t, J = 19.9 Hz), 32.8, 30.1 (t, J = 3.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.22 – -122.46 (m).

HRMS (EI) *m/z* calcd for $C_{17}H_{17}F_2N[M^+]$: 273.1329, found: 273.1323.



16

3-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)thiophene (**16**) (36.9 mg, 67%); yellow oil.

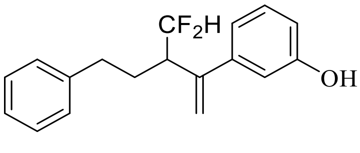
R_f =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 6.9 Hz, 1H), 7.25 (s, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 7.03 – 6.93 (m, 2H), 5.82 (td, J = 56.6, 4.2 Hz, 1H), 5.73 (s, 1H), 5.22 (s, 1H), 3.14 – 2.95 (m, 1H), 2.82 – 2.71 (m, 1H), 2.68 – 2.56 (m, 1H), 2.26 – 2.11 (m, 1H), 2.08 – 1.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.4, 138.1 (t, J = 4.4 Hz), 128.6, 128.6, 127.7, 126.2, 125.1, 124.0, 117.6 (t, J = 245.9 Hz), 114.7, 47.7 (t, J = 20.2 Hz), 32.9, 29.6 (t, J = 3.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.58 – -123.45 (m).

HRMS (EI) *m/z* calcd for $C_{16}H_{16}F_2S[M^+]$: 278.0941, found: 278.0934.



17

3-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)phenol (**17**) (38.7 mg, 67%); yellow oil.

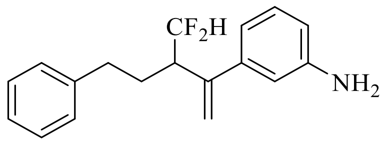
R_f =0.4 (petroleum ether: ethyl acetate, 10:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.78 (dd, *J* = 7.9, 2.6 Hz, 1H), 6.73 (t, *J* = 2.2 Hz, 1H), 5.78 (td, *J* = 56.5, 4.4 Hz, 1H), 5.56 (s, 1H), 5.30 (s, 1H), 4.85 (s, 1H), 3.08 – 2.92 (m, 1H), 2.83 – 2.71 (m, 1H), 2.68 – 2.53 (m, 1H)., 2.31 – 2.09 (m, 1H), 2.03 – 1.86 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.7, 145.1 (t, *J* = 4.3 Hz), 143.9, 141.5, 129.8, 128.6, 128.6, 126.2, 119.3, 118.0 (t, *J* = 244.2 Hz), 116.5, 114.8, 113.7, 47.5 (t, *J* = 20.0 Hz), 33.0, 30.1 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.02 – -128.86 (m).

HRMS (EI) *m/z* calcd for $C_{18}H_{18}F_2O[M^+]$: 288.1320, found: 288.1324.



18

3-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)aniline (**18**) (49.5 mg, 86%); yellow liquid.

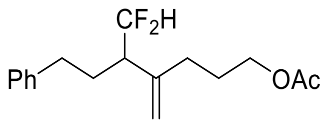
R_f =0.6 (petroleum ether: ethyl acetate, 10:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, *J* = 7.0 Hz, 1H), 7.41 (s, 1H), 7.39 – 7.31 (m, 1H), 7.33 – 7.24 (m, 3H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.74 (t, *J* = 2.0 Hz, 1H), 5.92 (td, *J* = 56.6, 4.3 Hz, 1H), 5.69 (s, 1H), 5.42 (s, 1H), 3.84 (s, 2H), 3.21 – 3.06 (m, 1H), 3.00 – 2.89 (m, 1H), 2.84 – 2.70 (m, 1H), 2.36 – 2.24 (m, 1H), 2.15 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.5, 145.6 (t, *J* = 4.1 Hz), 143.4, 141.6, 129.5, 128.6, 128.6, 126.1, 118.0 (t, *J* = 244.9 Hz), 117.2, 116.0, 114.7, 113.5, 47.6 (t, *J* = 19.8 Hz), 33.0, 29.8 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.53 – -124.53 (m).

HRMS (EI) *m/z* calcd for $C_{18}H_{19}F_2N[M^+]$: 287.1486, found: 287.1479.



19

5-(difluoromethyl)-4-methylene-7-phenylheptyl acetate (**19**) (51.0 mg, 86%); colorless liquid.

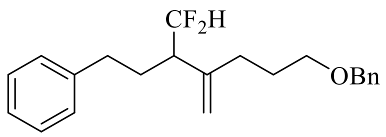
R$_f$ =0.7 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 2H), 5.64 (td, *J* = 56.7, 4.6 Hz, 1H), 5.05 (s, 1H), 4.99 (s, 1H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.64 (td, *J* = 9.8, 5.0 Hz, 1H), 2.54 – 2.39 (m, 2H), 2.10 – 2.02 (m, 2H), 2.01 (s, 3H), 1.99 – 1.90 (m, 1H), 1.81 – 1.71 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 171.3, 144.1 (t, *J* = 3.8 Hz), 141.5, 128.6, 128.5, 126.2, 118.2 (t, *J* = 244.5 Hz), 114.1, 64.0, 49.4 (t, *J* = 19.3 Hz), 33.0, 31.6, 28.9 (t, *J* = 4.0 Hz), 26.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ -117.37 – -121.87 (m).

HRMS (EI) *m/z* calcd for $C_{17}H_{23}F_2O_2[M^+]$: 296.1582, found:296.1587.



20

(7-(benzyloxy)-3-(difluoromethyl)-4-methyleneheptyl)benzene (**20**) (48.1 mg, 70%); colorless liquid.

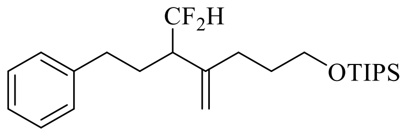
R$_f$ =0.6 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (t, *J* = 3.8 Hz, 4H), 7.26 – 7.21 (m, 3H), 7.17 (dd, *J* = 7.1, 2.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 5.65 (td, *J* = 56.8, 4.3 Hz, 1H), 5.05 (s, 1H), 4.97 (s, 1H), 4.48 (d, *J* = 2.8 Hz, 2H), 3.50 – 3.45 (m, 2H), 2.71 – 2.58 (m, 1H), 2.53 – 2.37 (m, 2H), 2.19 – 2.03 (m, 2H), 2.02 – 1.89 (m, 1H), 1.85 – 1.67 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.7 (t, *J* = 3.8 Hz)., 141.6, 138.6, 128.6, 128.5, 128.5, 127.8, 127.7, 118.2 (t, *J* = 245.4 Hz), 113.8, 73.1, 69.9, 49.6 (t, *J* = 19.2 Hz), 33.0, 31.9, 29.0 (t, *J* = 4.2 Hz), 27.7.

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.48 – -124.15 (m).

HRMS (ESI) *m/z* calcd for $C_{22}H_{26}F_2O$[M$^+$]: 344.1946, found:344.1949.



21

((5-(difluoromethyl)-4-methylene-7-phenylheptyl)oxy)triisopropylsilane (**21**) (66.1 mg, 81%); white solid.

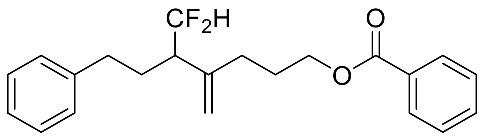
R$_f$ =0.6 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.15 (m, 3H), 5.70 (td, *J* = 56.7, 4.7 Hz, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.74 – 2.63 (m, 1H), 2.60 – 2.41 (m, 2H), 2.25 – 2.06 (m, 2H), 2.04 – 1.94 (m, 1H), 1.90 – 1.79 (m, 1H), 1.76 – 1.64 (m, 2H), 1.06 (d, *J* = 4.7 Hz, 21H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0 (t, *J* = 3.8 Hz), 141.7, 128.6, 128.5, 126.1, 118.2 (t, *J* = 244.3 Hz), 113.7, 62.9, 49.7 (t, *J* = 19.2 Hz), 33.1, 31.5, 31.0, 29.0 (t, *J* = 4.2 Hz), 18.2, 12.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -112.81 – -134.61 (m).

HRMS (EI) *m/z* calcd for $C_{24}H_{40}F_2OSi$[M$^+$]: 410.2811, found: 410.2814.



22

5-(difluoromethyl)-4-methylene-7-phenylheptyl benzoate (**22**) (57.3 mg, 80%); colorless liquid.

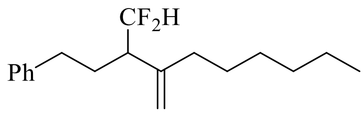
R$_f$ =0.4 (petroleum ether: ethyl acetate, 30:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.19 – 7.08 (m, 3H), 5.68 (td, *J* = 56.7, 4.6 Hz, 1H), 5.12 (s, 1H), 5.04 (s, 1H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.73 – 2.63 (m, 1H), 2.59 – 2.44 (m, 2H), 2.30 – 2.09 (m, 2H), 2.06 – 1.89 (m, 3H), 1.86 – 1.76 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.7, 144.1 (t, *J* = 3.8 Hz), 141.5, 133.1, 130.4, 129.7, 128.6, 128.5, 128.5, 126.1, 118.2 (t, *J* = 244.5 Hz), 114.3, 64.5, 49.4 (t, *J* = 19.2 Hz), 33.00, 31.7, 29.04 (t, *J* = 4.3 Hz), 26.7.

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.73 – -133.05 (m).

HRMS (ESI) *m/z* calcd for $C_{22}H_{25}F_2O_2[(M+H)^+]$: 359.1817, found: 359.1825.



23

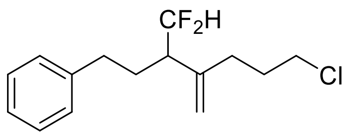
1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-ethylbenzene (**23**)[1] (35.4 mg, 64%); colorless liquid.

R$_f$ =0.6 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (m, 3H), 5.69 (td, *J* = 56.8, 4.7 Hz, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 2.75 – 2.63 (m, 1H), 2.60 – 2.50 (m, 1H), 2.52 – 2.38 (m, 1H), 2.10 – 1.94 (m, 3H), 1.87 - 1.72 (m, 1H), 1.53 – 1.41 (m, 2H), 1.37 – 1.24 (m, 6H), 0.95 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.4 (t, *J* = 3.8 Hz), 141.7, 128.6, 128.5, 126.1, 118.3(t, *J* = 244.4 Hz), 113.4, 49.5 (t, *J* = 19.1 Hz), 35.6, 33.1, 31.9, 29.2, 29.0 (t, *J* = 4.2 Hz), 27.5, 22.8, 14.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.65 – -122.42 (m).



24

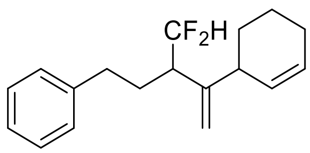
(7-chloro-3-(difluoromethyl)-4-methyleneheptyl)benzene (**24**)[1] (31.1 mg, 58%); yellow oil.

Rf =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.14 (m, 3H), 5.70 (td, *J* = 56.7, 4.7 Hz, 1H), 5.07 (d, *J* = 23.4 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.62 – 2.39 (m, 2H), 2.30 – 2.14 (m, 1H), 2.05 – 1.76 (m, 4H), 1.72 – 1.63 (m, 1H), 1.56 – 1.52 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 143.6 (t, *J* = 3.6 Hz), 141.3, 128.5, 128.4, 126.1, 118.0 (t, *J* = 244.3 Hz), 114.3, 49.3 (t, *J* = 19.5 Hz), 44.4, 32.9, 32.3, 30.2, 29.0 (t, *J* = 4.1 Hz).

^{19}F NMR (377 MHz, CDCl$_3$) δ -103.87 – -128.72 (m).



25

(4-(cyclohex-2-en-1-yl)-3-(difluoromethyl)pent-4-en-1-yl)benzene (**25**) (39.4 mg, 71%); colorless liquid.

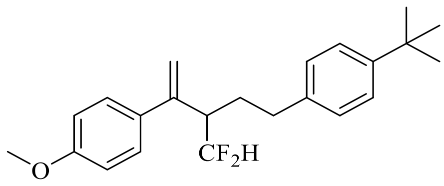
R$_f$ =0.5 (petroleum ether, v/v).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, *J* = 7.1 Hz, 1H), 7.26 (s, 1H), 7.19 (d, *J* = 6.9 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 5.79 (s, 1H), 5.71 (td, *J* = 56.8, 3.9 Hz, 1H), 5.31 (s, 1H), 5.03 (s, 1H), 2.99 – 2.84 (m, 1H), δ 2.74 – 2.63 (m, 1H), 2.61 – 2.49 (m, 1H), 2.23 – 2.15 (m, 3H), 2.16 – 2.08 (m, 3H), 1.92 – 1.82 (m, 1H), 1.73 – 1.66 (m, 2H), 1.62 – 1.57 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.3 (dd, *J* = 5.6, 3.3 Hz), 141.9, 136.7, 128.6, 128.5, 126.1, 125.0, 118.3 (t, *J* = 244.9 Hz), 111.4, 43.8 (t, *J* = 19.5 Hz), 33.0, 30.1 (t, *J* = 4.0 Hz), 26.7, 26.0, 23.0, 22.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.34 – -126.14 (m).

HRMS (EI) *m/z* calcd for $C_{18}H_{22}F_2$[M^+]: 276.1684, found:276.1681.



26

1-(tert-butyl)-4-(3-(difluoromethyl)-4-(4-methoxyphenyl)pent-4-en-1-yl)benzene (**26**) (55.1 mg, 77%); white soild.

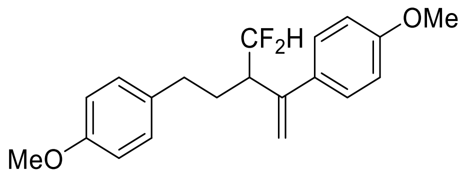
R_f =0.2 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.91 – 6.84 (m, 2H), 5.78 (td, *J* = 56.6, 4.5 Hz, 1H), 5.50 (s, 1H), δ 5.23 (s, 1H), 3.83 (s, 3H), 3.11 – 2.97 (m, 1H), 2.81 – 2.68 (m, 1H), 2.65 – 2.53 (m, 1H), 2.20 – 2.09 (m, 1H), 2.01 – 1.89 (m, 1H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 149.0, 144.8 (t, *J* = 4.3 Hz), 138.5, 134.6, 128.2, 127.8, 125.4, 118.1 (t, *J* = 244.4 Hz), 114.9, 113.9, 55.4, 47.7 (t, *J* = 19.8 Hz), 34.5, 32.4, 31.5, 30.0 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.59 – -124.69 (m).

HRMS (ESI) *m/z* calcd for $C_{23}H_{28}F_2O[M^+]$: 358.2103, found: 358.2100.



27

1-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-4-ethylbenzene (**27**) (42.5 mg, 64%); colorless liquid.

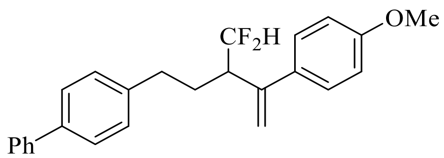
R_f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.06 – 6.99 (m, 2H), 6.91 – 6.85 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.76 (td, *J* = 56.7, 4.4 Hz, 1H), 5.50 (s, 1H), 5.22 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.15 – 2.95 (m, 1H), 2.78 – 2.65 (m, 1H), 2.62 – 2.46 (m, 1H), 2.19 – 2.00 (m, 1H), 1.98 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.4, 158.0, 144.8 (t, J = 4.4 Hz), 134.6, 133.6, 129.5, 127.8, 118.1 (t, J = 244.9 Hz), 114.9, 113.9, 55.4, 55.4, 47.5 (t, J = 19.7 Hz), 32.0, 30.3 (t, J = 3.8 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -115.01 – -129.07 (m).

HRMS (EI) *m/z* calcd for $C_{20}H_{22}F_2O_2$[M$^+$]: 332.1582, found: 332.1579.



28

4-(3-(difluoromethyl)-4-(4-methoxyphenyl)pent-4-en-1-yl)-1,1'-biphenyl (**28**) (62.7 mg, 83%); white solid.

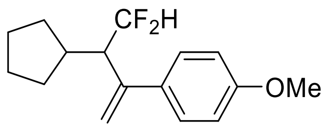
R$_f$ =0.4 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, J = 7.0 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.79 (td, J = 56.6, 4.4 Hz, 1H), 5.52 (s, 1H), 5.25 (s, 1H), 3.82 (s, 3H), 3.11 – 2.95 (m, 1H), 2.89 – 2.75 (m, 1H), 2.71 – 2.58 (m, 1H), 2.27 – 2.11 (m, 1H), 2.07 – 1.90 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.5, 144.8 (t, J = 4.1 Hz), 141.1, 140.7, 139.1, 134.5, 129.0, 128.9, 127.8, 127.3, 127.2, 127.1, 118.1 (t, J = 244.2 Hz), 115.0, 114.0, 55.5, 47.5 (t, J = 19.8 Hz), 32.6, 30.1 (t, J = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -116.65 – -122.88 (m).

HRMS (EI) *m/z* calcd for $C_{25}H_{24}F_2O$[M$^+$]: 378.1795, found: 378.1788.



29

1-(3-cyclopentyl-4,4-difluorobut-1-en-2-yl)-4-methoxybenzene (**29**) (39.0 mg, 73%); colorless liquid.

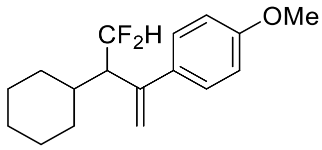
R$_f$ =0.5 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 6.89 – 6.82 (m, 2H), 5.89 (td, *J* = 56.5, 3.9 Hz, 1H), 5.41 (s, 1H), 5.18 (s, 1H), 3.81 (s, 3H), 2.99 – 2.56 (m, 1H), 2.23 – 2.07 (m, 1H), 2.01 – 1.90 (m, 1H), 1.87 – 1.78 (m, 1H), 1.75 – 1.64 (m, 1H), 1.62 – 1.57 (m, 1H), 1.53 – 1.41 (m, 1H), 1.34 – 1.21 (m, 2H), 1.16 – 1.02 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.2, 145.6 (t, *J* = 3.9 Hz), 135.9, 127.8, 118.2 (t, *J* = 244.0 Hz), 115.2, 113.8, 55.4, 53.6 (t, *J* = 18.7 Hz), 41.4 (t, *J* = 3.6 Hz), 31.7, 31.5, 25.4, 24.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -117.96 – -120.20 (m).

HRMS (EI) *m/z* calcd for $C_{16}H_{20}F_2O$[M$^+$]: 266.1482, found: 266.1477.



30

1-(3-cyclohexyl-4,4-difluorobut-1-en-2-yl)-4-methoxybenzene (**30**) (43.4 mg, 78%); colorless liquid.

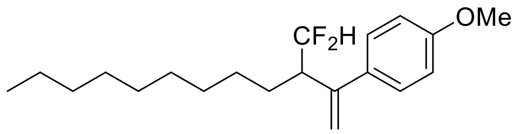
R$_f$ =0.4 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.00 (td, *J* = 56.4, 4.2 Hz, 1H), 5.42 (s, 1H), 5.15 (s, 1H), 3.81 (s, 3H), 2.85 – 2.69 (m, 1H), 1.94 – 1.62 (m, 5H), 1.34 – 0.92 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.2, 144.7 (t, *J* = 4.0 Hz), 136.3, 127.7, 117.8 (t, *J* = 243.9 Hz), 114.8, 113.8, 55.4, 53.5 (t, *J* = 18.7 Hz), 39.4, 31.3, 31.1, 26.5, 26.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ -118.19 – -121.91 (m).

HRMS (EI) *m/z* calcd for $C_{17}H_{22}F_2O$[M$^+$]: 280.1633, found: 280.1630.



31

1-(3-(difluoromethyl)dodec-1-en-2-yl)-4-methoxybenzene (**31**) (44.1 mg, 68%); colorless liquid.

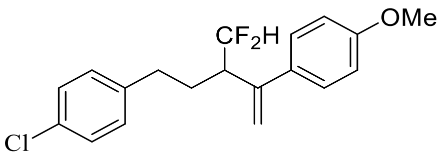
R_f =0.7 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 6.92 – 6.81 (m, 2H), 5.74 (td, *J* = 56.8, 4.7 Hz, 1H), 5.41 (s, 1H), 5.15 (s, 1H), 3.82 (s, 3H), 3.06 – 2.86 (m, 1H), 1.84 – 1.70 (m, 1H), 1.65 – 1.54 (m, 1H), 1.44 – 1.37 (m, 1H), 1.31 – 1.18 (m, 13H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.3, 145.3 (t, *J* = 4.5 Hz), 135.0, 127.8, 118.3 (t, *J* = 244.5 Hz), 114.6, 113.9, 55.4, 48.4 (t, *J* = 20.2 Hz), 32.0, 29.8, 29.7, 29.5, 29.4, 28.7 (t, *J* = 4.0 Hz), 26.9, 22.8, 14.3.

^{19}F NMR (376 MHz, CDCl$_3$) δ -111.75 – -125.74 (m).

HRMS (EI) *m/z* calcd for $C_{20}H_{30}F_2O$[M$^+$]: 324.2265, found: 324.2259.



32

1-chloro-3-(3-(difluoromethyl)-4-(4-methoxyphenyl)pent-4-en-1-yl)benzene (**32**) (47.8 mg, 71%); yellow oil.

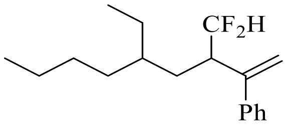
R_f =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (s, 2H), 7.26 – 7.22 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.89 (dd, *J* = 8.6, 1.7 Hz, 2H), 5.79 (td, *J* = 56.7, 4.4 Hz, 1H), 5.51 (s, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 3.07 – 2.90 (m, 1H), 2.81 – 2.69 (m, 1H), 2.65 – 2.53 (m, 1H), 2.18 – 2.05 (m, 1H), 1.93 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.4, 144.6 (t, *J* = 4.2 Hz), 139.8, 134.3, 131.8, 129.8, 128.5, 127.7, 117.9 (t, *J* = 244.9 Hz), 114.8, 113.9, 55.3, 47.3 (t, *J* = 19.9 Hz), 32.2, 29.9 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -108.63 – -157.97 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{19}ClF_2O$[M$^+$]: 336.1093, found: 336.1088.



33

(3-(difluoromethyl)-4-ethyloct-1-en-2-yl)benzene (**33**) (48.2 mg, 87%); colorless liquid.

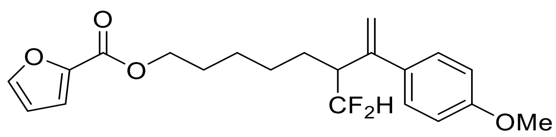
R$_f$ =0.7 (petroleum ether)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.22 (m, 5H), 5.76 (td, *J* = 56.9, 2.3 Hz, 1H), 5.50 (s, 1H), 5.26 (s, 1H), 3.20 – 2.94 (m, 1H), 1.63 (t, *J* = 7.1 Hz, 2H), 1.45 – 1.29 (m, 3H), 1.29 – 1.10 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 2H), 0.88 – 0.78 (m, 3H), 0.78 (d, *J* = 7.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.1 (dt, *J* = 5.9, 4.3 Hz), 142.6 (d, *J* = 3.0 Hz), 128.5, 127.7, 126.7, 117.3 (t, *J* = 244.4 Hz), 116.4, 46.1 (t, *J* = 19.5 Hz), 35.6 (d, *J* = 38.2 Hz), 32.8 (d, *J* = 113.9 Hz), 32.5 (dt, *J* = 25.1, 3.7 Hz), 28.6 (d, *J* = 48.4 Hz), 26.6, 25.1, 23.1, 14.2 (d, *J* = 5.9 Hz), 10.9, 10.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -118.09 – -123.18 (m).

HRMS (EI) *m/z* calcd for $C_{18}H_{26}F_2[M^+]$: 280.1997, found:280.1994.



34

6-(difluoromethyl)-7-(4-methoxyphenyl)oct-7-en-1-yl furan-2-carboxylate (**34**) (53.4 mg, 71%); yellow soild.

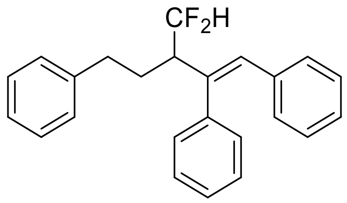
R$_f$ =0.4 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, *J* = 1.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.14 (d, *J* = 3.4 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.75 (td, *J* = 56.7, 4.6 Hz, 1H), 5.42 (s, 1H), 5.15 (s, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 3.81 (s, 3H), 3.12 – 2.87 (m, 1H), 1.90 – 1.57 (m, 4H), 1.51 – 1.32 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.4, 159.0, 146.4, 145.1 (t, *J* = 4.4 Hz), 144.9, 134.8, 127.7, 118.2 (t, *J* = 245.4 Hz), 117.9, 114.7, 113.9, 111.9, 65.0, 55.4, 48.3 (t, *J* = 19.6 Hz), 28.6, 28.5 (t, *J* = 4.0 Hz), 26.6, 26.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -114.90 – -124.28 (m).

HRMS (EI) *m/z* calcd for $C_{21}H_{24}F_2O_4[M^+]$: 378.1643, found: 378.1639.



35

(Z)-(3-(difluoromethyl)pent-1-ene-1,2,5-triyl)tribenzene (**35**) (60.1 mg, 87%); white solid.

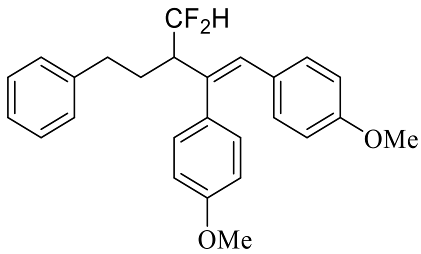
R$_f$ =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.32 (m, 5H), 7.29 (d, *J* = 6.3 Hz, 1H), 7.25 – 7.21 (m, 4H), 7.15 (dt, *J* = 6.1, 2.6 Hz, 3H), 6.97 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.64 (s, 1H), 5.79 (td, *J* = 56.5, 5.4 Hz, 1H), 3.03 – 2.87 (m, 2H), 2.83 – 2.71 (m, 1H), 2.16 – 2.08 (m, 1H), 2.05 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.4, 139.6, 137.8 (dd, *J* = 5.4, 3.5 Hz), 136.4, 131.7, 129.3, 129.0, 129.0, 128.5, 128.5, 128.0, 127.6, 127.0, 126.2, 117.6 (t, *J* = 243.8 Hz), 52.6 (t, *J* = 20.0 Hz), 33.1, 28.7 (t, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -112.25 – -136.46 (m).

HRMS (EI) *m/z* calcd for $C_{24}H_{22}F_2$[M^+]: 348.1684, found: 348.1680.



36

(Z)-4,4'-(3-(difluoromethyl)-5-phenylpent-1-ene-1,2-diyl)bis(methoxybenzene) (**36**) (52.1 mg, 64%); white solid.

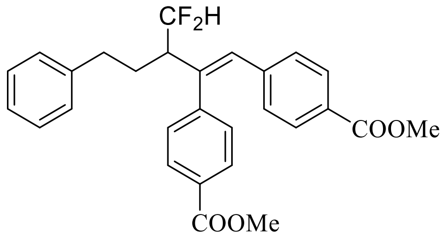
R$_f$ =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.91 – 6.81 (m, 4H), 6.66 (d, *J* = 8.3 Hz, 2H), 6.47 (s, 1H), 5.69 (td, *J* = 56.5, 5.4 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 2.95 – 2.78 (m, 2H), 2.73 – 2.62 (m, 1H), 2.08 – 1.98 (m, 1H), 1.93 – 1.86 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.0, 158.5, 141.6, 132.0, 131.2, 130.6, 130.4, 129.3, 128.6, 128.6, 126.2, 117.9 (t, *J* = 244.4 Hz), 114.5, 113.5, 55.4, 55.3, 52.9 (t, *J* = 19.8 Hz), 33.2, 29.9, 28.7 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -110.54 – -139.01 (m).

HRMS (EI) *m/z* calcd for $C_{26}H_{26}F_2O_2$[M^+]: 408.1901, found: 408.1895.



37

Dimethyl 4,4'-(3-(difluoromethyl)-5-phenylpent-1-ene-1,2-diyl)(Z)-dibenzoate (**37**) (67.1 mg, 73%); yellow solid.

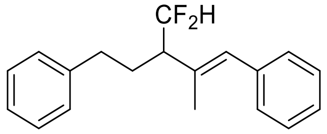
R$_f$ =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.82 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.28 (s, 1H), 7.26 (d, *J* = 14.2 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.74 (s, 1H). 5.68 (td, *J* = 56.3, 5.0 Hz, 1H), 3.86 (d, *J* = 1.3 Hz, 3H), 3.79 (d, *J* = 1.3 Hz, 3H), 2.92 – 2.75 (m, 2H), 2.70 – 2.58 (m, 1H), 2.11 – 1.96 (m, 1H), 1.97 – 1.83 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.8, 166.8, 144.5, 140.9, 140.7, 139.6 (t, *J* = 3.0 Hz), 131.5, 130.3, 129.7, 129.5, 129.3, 129.2, 128.7, 128.5, 126.4, 117.4 (t, *J* = 245.4 Hz), 52.4, 52.2, 52.1, 51.9, 33.1, 29.1(t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -103.73 – -131.70 (m).

HRMS (EI) *m/z* calcd for $C_{28}H_{26}F_2O_4$[M^+]: 464.1794, found:464.1792.



38

(E)-(3-(difluoromethyl)-2-methylpent-1-ene-1,5-diyl)dibenzene (**38**) (40.6 mg, 71%, dr = 14:1); yellow solid.

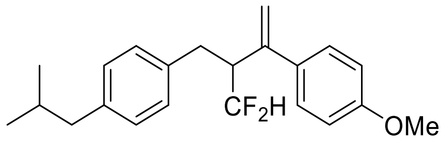
R$_f$ =0.6 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 3H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 5.8 – 5.7 (m, 1H), 5.64 (td, *J* = 56.7, 5.4 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.78 – 2.70 (m, 1H), 2.66 – 2.58 (m, 1H), 2.00 – 1.94 (m, 1H), 1.86 – 1.75 (m, 1H), 1.58 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.7, 139.5, 137.2 (dd, *J* = 5.4, 3.6 Hz), 129.1, 128.6, 128.5, 128.5, 127.4, 127.1, 126.1, 117.9 (t, *J* = 243.4 Hz), 51.5 (t, *J* = 19.8 Hz), 33.2, 28.8 (t, *J* = 4.0 Hz), 15.0.

^{19}F NMR (376 MHz, CDCl$_3$) δ -114.66 – -124.87 (m).

HRMS (EI) *m/z* calcd for $C_{19}H_{20}F_2$[M$^+$]: 286.1533, found: 286.1530.



39

1-(4,4-difluoro-3-(4-isobutylbenzyl)but-1-en-2-yl)-4-methoxybenzene (**39**) (53.3 mg, 78%); white solid.

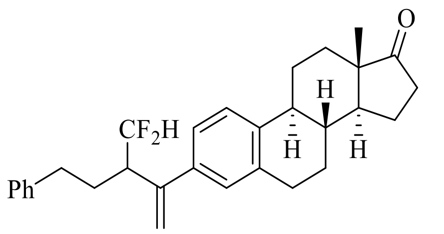
R$_f$ =0.5 (petroleum ether: ethyl acetate, 100:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 – 7.06 (m, 3H), 7.06 – 7.00 (m, 3H), 6.82 – 6.73 (m, 2H), 5.81 (td, *J* = 56.5, 4.1 Hz, 1H), 5.44 (s, 1H), 5.25 (s, 1H), 3.78 (s, 3H), 3.3 – 3.2 (m, 1H), 3.11 (dd, *J* = 13.8, 5.3 Hz, 1H), 2.89 (dd, *J* = 13.8, 9.4 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.82 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.88 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.2, 144.6 (t, *J* = 3.8 Hz), 139.9, 135.8, 135.1, 129.3, 129.1, 127.7, 117.6 (t, *J* = 244.2 Hz), 115.6, 113.7, 55.4, 50.2 (t, *J* = 19.5 Hz), 45.1, 34.7 (t, *J* = 4.6 Hz), 30.4, 22.5, 22.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ -119.14 – -123.82 (m).

HRMS (EI) *m/z* calcd for $C_{22}H_{26}F_2O$[M$^+$]: 344.1952, found: 344.1944.



40

(8R,9S,13S,14S)-3-(3-(difluoromethyl)-5-phenylpent-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**40**) (47.6 mg, 53%); white solid.

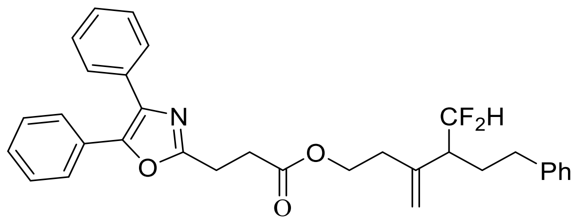
R$_f$ =0.5 (petroleum ether: ethyl acetate, 50:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (dd, *J* = 9.0, 1.8 Hz, 2H), 7.25 (s, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.10 (m, 3H), 7.02 (dd, *J* = 5.2, 2.0 Hz, 1H), 5.76 (tdd, *J* = 56.6, 4.5, 2.3 Hz, 1H), 5.55 (s, 1H), 5.27 (s, 1H), 3.09 – 2.98 (m, 1H), 2.92 – 2.85 (m, 2H), 2.77 (dt, *J* = 10.6, 3.7 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.54 – 2.45 (m, 1H), 2.46 – 2.41 (m, 1H), 2.31 (td, *J* = 11.1, 4.1 Hz, 1H), 2.20 – 2.10 (m, 2H), 2.10 – 2.02 (m, 2H), 1.99 – 1.91 (m, 2H), 1.68 – 1.59 (m, 2H), 1.56 – 1.40 (m, 5H), 1.34 – 1.22 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.1 (t, *J* = 3.7 Hz), 141.6, 139.6, 136.7, 128.6, 128.6, 127.2, 127.2, 126.2, 125.6, 124.1, 124.1, 118.0 (t, *J* = 244.3 Hz), 115.7, 50.6, 48.1, 47.4 (t, *J* = 19.7 Hz), 44.5, 38.3, 36.0, 33.0, 31.7, 30.0 (t, *J* = 4.5 Hz), 29.6, 26.6, 25.8, 21.7, 14.0.

^{19}F NMR (376 MHz, CDCl$_3$) δ -117.07 – -122.98 (m).

HRMS (EI) *m/z* calcd for $C_{30}H_{34}F_2O$[M$^+$]: 448.2572, found:448.2568.



41

4-(difluoromethyl)-3-methylene-6-phenylhexyl3-(4,5-diphenyloxazol-2-yl)propanoate (**41**) (83.4 mg, 81%); white solid.

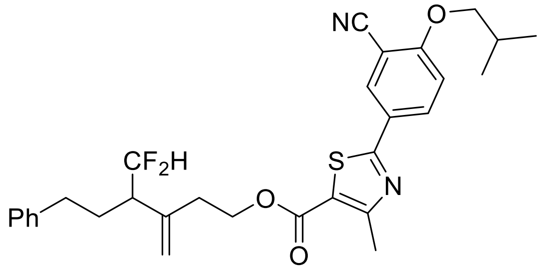
R$_f$ =0.4 (petroleum ether: ethyl acetate, 5:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.52 (m, 2H), 7.53 – 7.46 (m, 2H), 7.33 – 7.23 (m, 4H), 7.27 – 7.16 (m, 4H), 7.12 (d, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 2H), 5.60 (td, *J* = 56.6, 4.4 Hz, 1H), 5.05 (s, 1H), 4.99 (s, 1H), 4.21 (t, *J* = 6.9 Hz, 2H), 3.11 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.67 – 2.54 (m, 1H), 2.52 – 2.36 (m, 3H), 2.35 – 2.23 (m, 1H), 1.98 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.0, 161.8, 145.6, 141.3, 141.0 (t, *J* = 3.8 Hz), 135.3, 132.6, 129.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 128.0, 126.6, 126.2, 118.0 (t, *J* = 244.6 Hz), 116.1, 62.8, 49.4 (t, *J* = 19.3 Hz), 34.0, 32.9, 31.2, 28.8 (t, *J* = 4.0 Hz), 23.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ -117.71 – -121.49 (m).

HRMS (ESI) *m/z* calcd for $C_{32}H_{32}F_2NO_3$[(M+H)$^+$]: 516.2345, found: 516.2344.



42

4-(difluoromethyl)-3-methylene-6-phenylhexyl2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (**42**) (76.4 mg, 71%); yellow solid.

R$_f$ =0.3 (petroleum ether: ethyl acetate, 7:1, v/v)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 6.99 (d, *J* = 8.9 Hz, 1H), 5.74 (td, *J* = 56.5, 4.5 Hz, 1H), 5.23 (s, 1H), 5.15 (s, 1H), 4.45 (td, *J* = 6.7, 3.5 Hz, 2H), 3.89 (d, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 2.78 – 2.70 (m, 1H), 2.61 – 2.43 (m, 4H), 2.25 – 2.14 (m, 1H), 2.10 – 1.98 (m, 1H), 1.93 – 1.81 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.5, 162.6, 162.0, 161.6, 141.3, 140.8 (t, *J* = 3.8 Hz), 132.7, 132.2, 128.6, 128.5, 126.3, 126.0, 121.6, 118.0 (t, *J* = 244.5 Hz), 116.4, 115.5, 112.7, 103.1, 75.8, 63.1, 49.3 (t, *J* = 19.4 Hz), 34.3, 33.0, 28.9 (t, *J* = 4.0 Hz), 28.3, 19.2, 17.6.

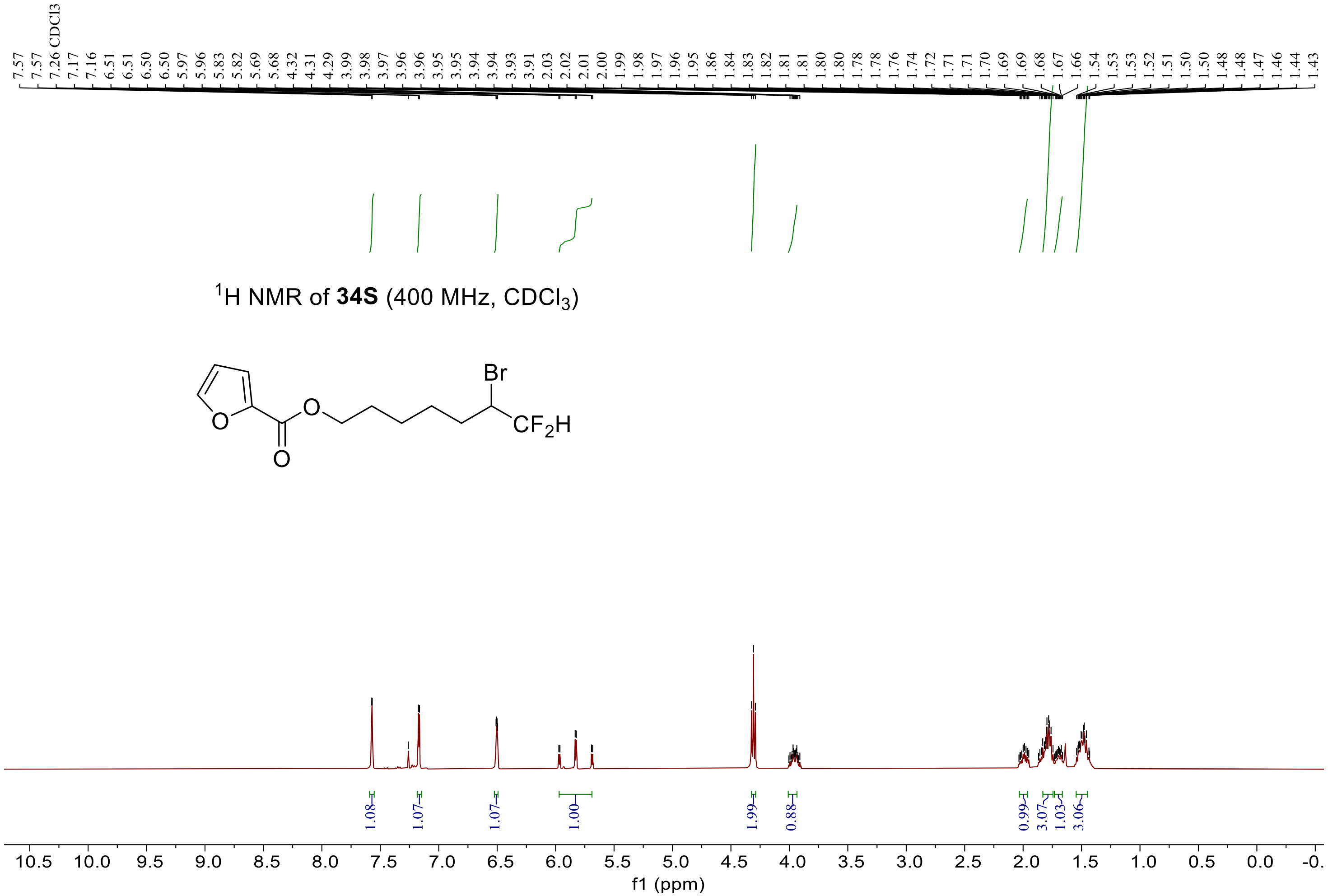
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.68 – -121.61 (m).

HRMS (ESI) *m/z* calcd for $C_{30}H_{33}F_2N_2O_3S$[(M+H)$^+$]: 539.2175, found: 539.2173.

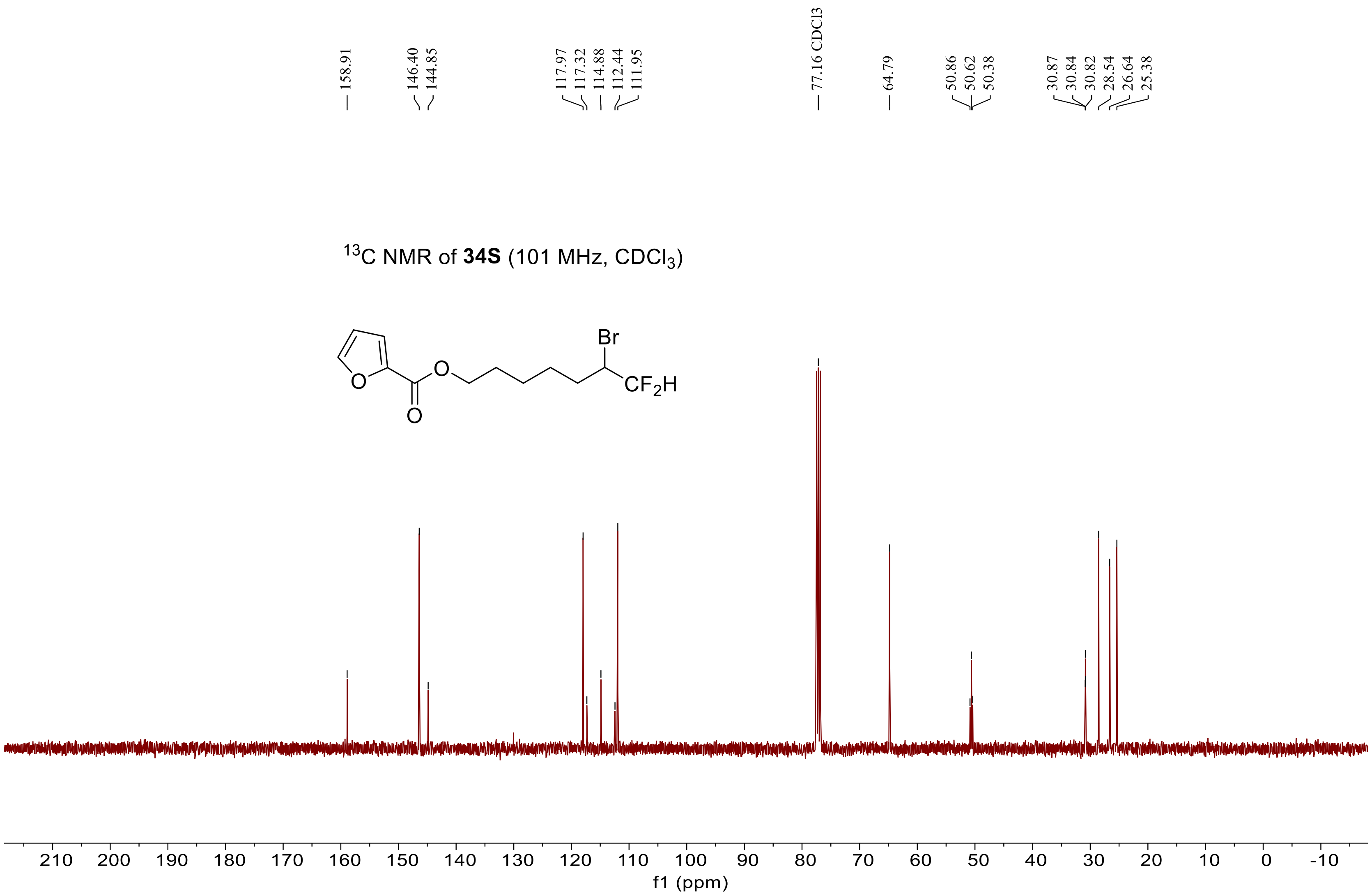
8. References

[1] Liu, B.; Dong, J.; Wang, H.; Chen, J.; Liu, S.; Xiong, X.; Yuan, Y.; Zeng, X., Nickel-catalyzed reductive cross-coupling of difluoromethylated secondary alkyl bromides with organohalides. *Chem Commun* **2025,** *61*, 2357-2360.
[2] Li, P.-P.; Yang, Z.; Cai, S.-Q.; Liang, W.; Fang, S.-C.; Zhao, J.-F.; Pan, B.; Du, F., Palladium-Catalyzed and Photoinduced Site-Selective Alkynylation and Oxidation of the Remote C(sp3)–H. *Org Lett* **2025,** *27*, 2602-2608.
[3] Bera, S.; Fan, C.; Hu, X., Enantio- and diastereoselective construction of vicinal C(sp3) centres via nickel-catalysed hydroalkylation of alkenes. *Nature Catalysis* **2022,** *5*, 1180-1187.
[4] Zhao, X.; Zhu, S.; Qing, F.-L.; Chu, L., Reductive hydrobenzylation of terminal alkynes via photoredox and nickel dual catalysis. *Chem Commun* **2021,** *57*, 9414-9417.
[5] (a) Zhang, Y.-Q.; Hu, L.; Yuwen, L.; Lu, G.; Zhang, Q.-W., Nickel-catalysed enantioselective hydrosulfenation of alkynes. *Nature Catalysis* **2023,** *6*, 487-494; (b) Zhang, Q.-Q.; Jin, R.-X.; Gao, Q.; Liu, P.; Zuo, Y.-W.; Lan, Q.; Wang, X.-S., Regioselective Nickel-Catalyzed Hydrotrifluoroalkylation of Alkynes to Construct Trisubstituted Allylic Trifluoromethyl Alkenes. *Org Lett* **2025,** *27*, 3765-3770; (c) Zhang, T.; Zuo, Y.-W.; Jin, R.-X.; Zhang, Y.-F.; Wu, B.-B.; Wang, X.-S., Nickel-Catalyzed Hydrotrifluoroalkylation of Alkynes to Construct Allylic Trifluoromethyl Terminal Alkenes. *Org Lett* **2023,** *25*, 3578-3584.

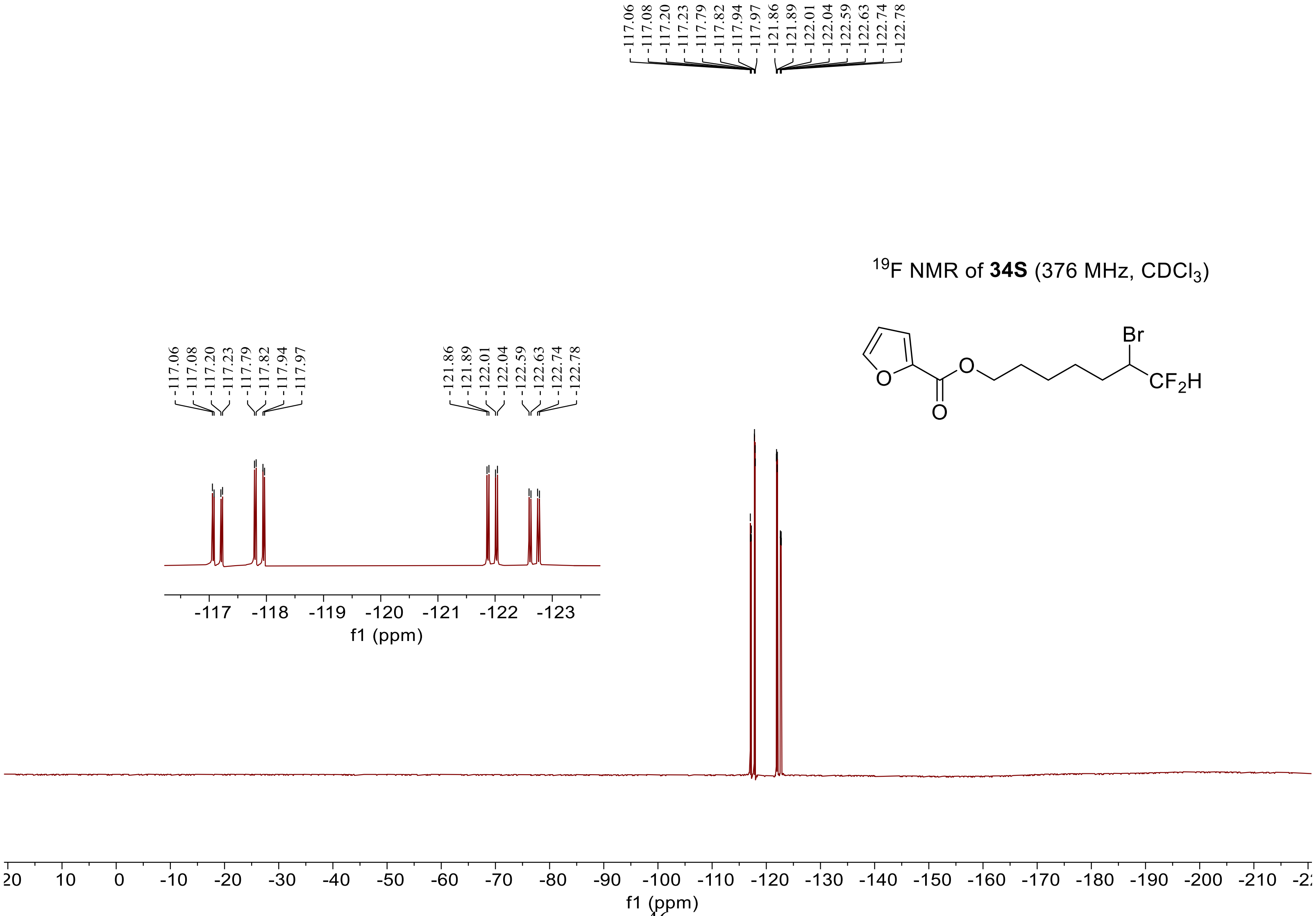
9. NMR Spectra



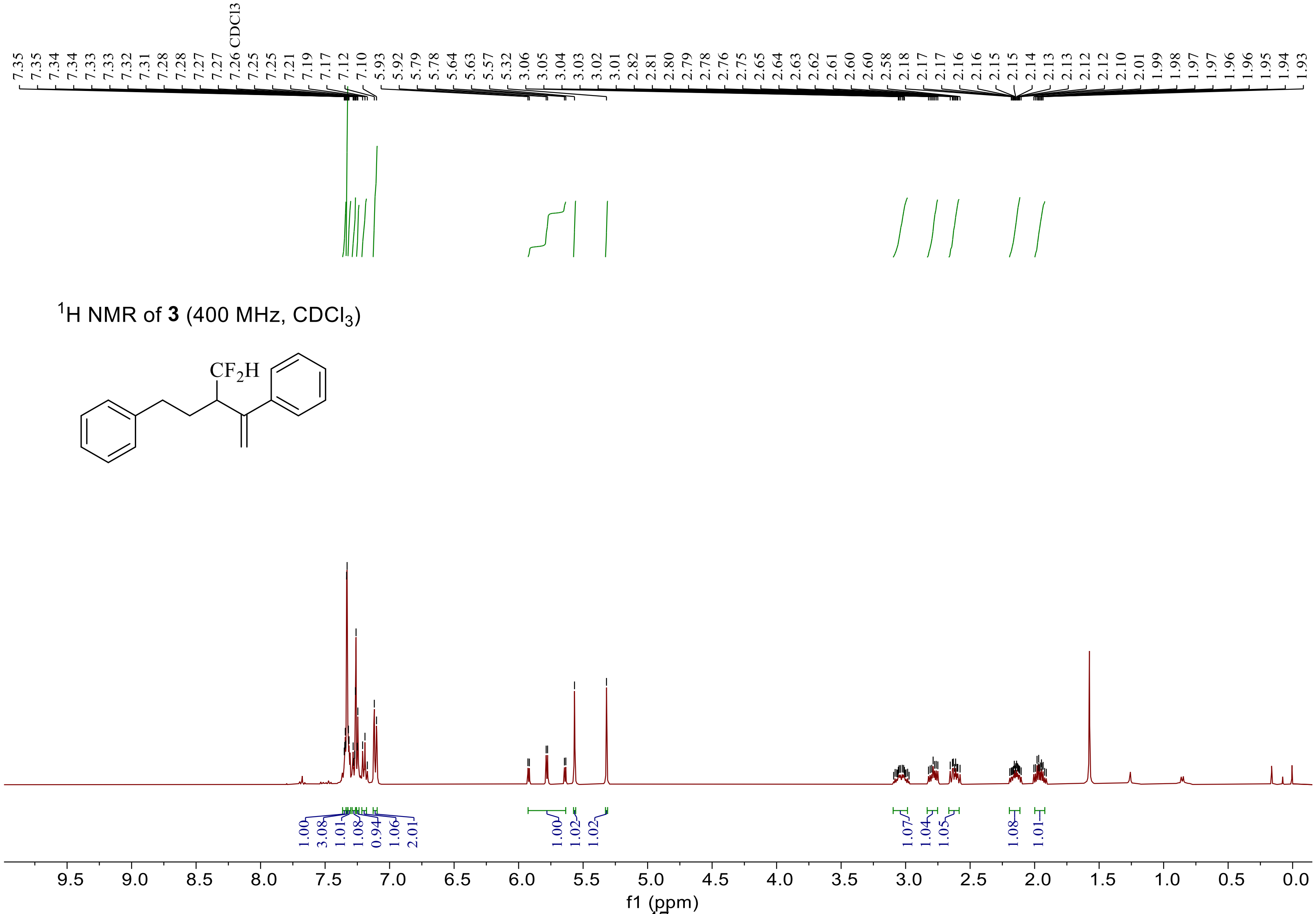
^{13}C NMR of **34S** (101 MHz, $CDCl_3$)

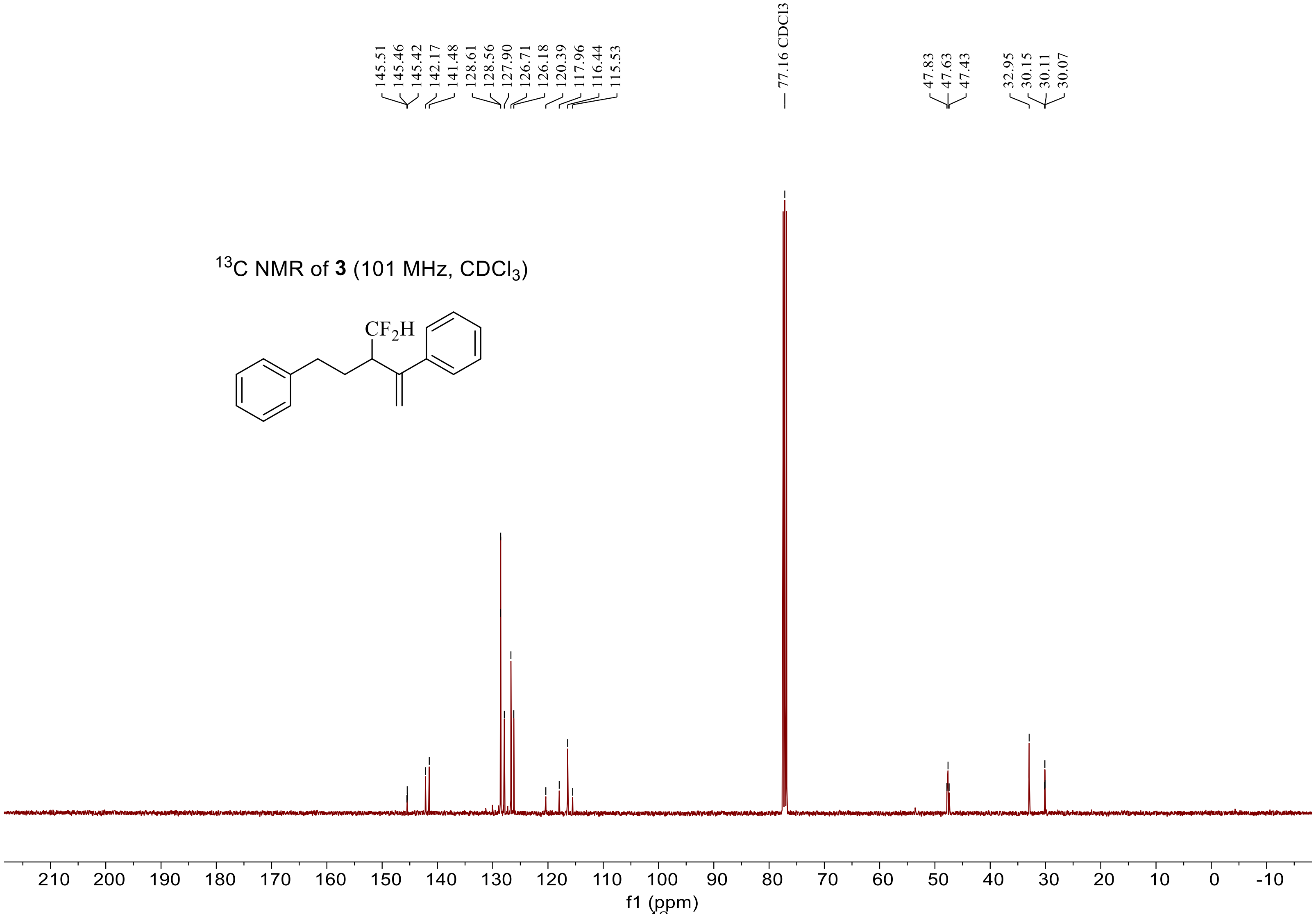


^{19}F NMR of **34S** (376 MHz, $CDCl_3$)

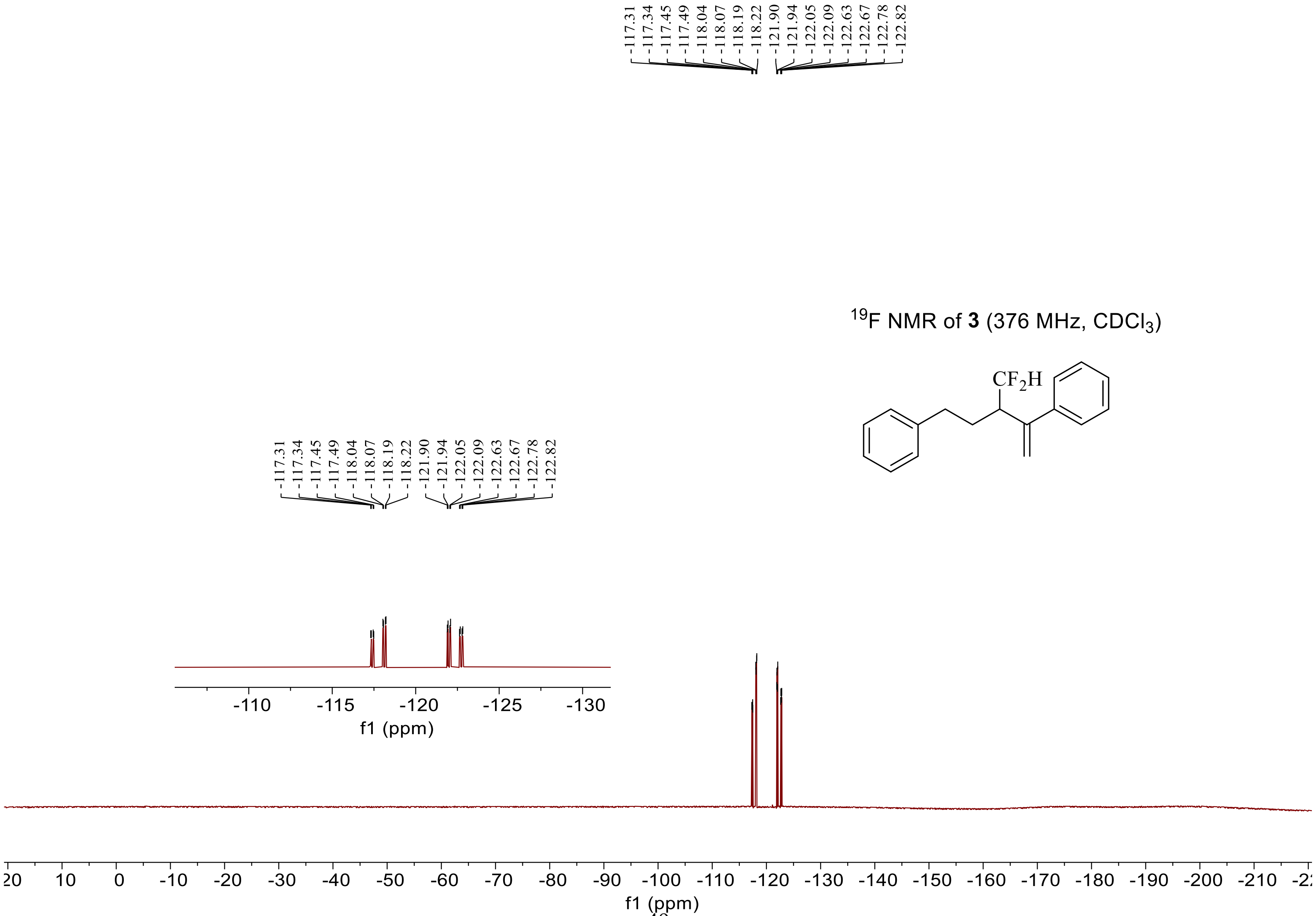


[1]H NMR of **3** (400 MHz, $CDCl_3$)

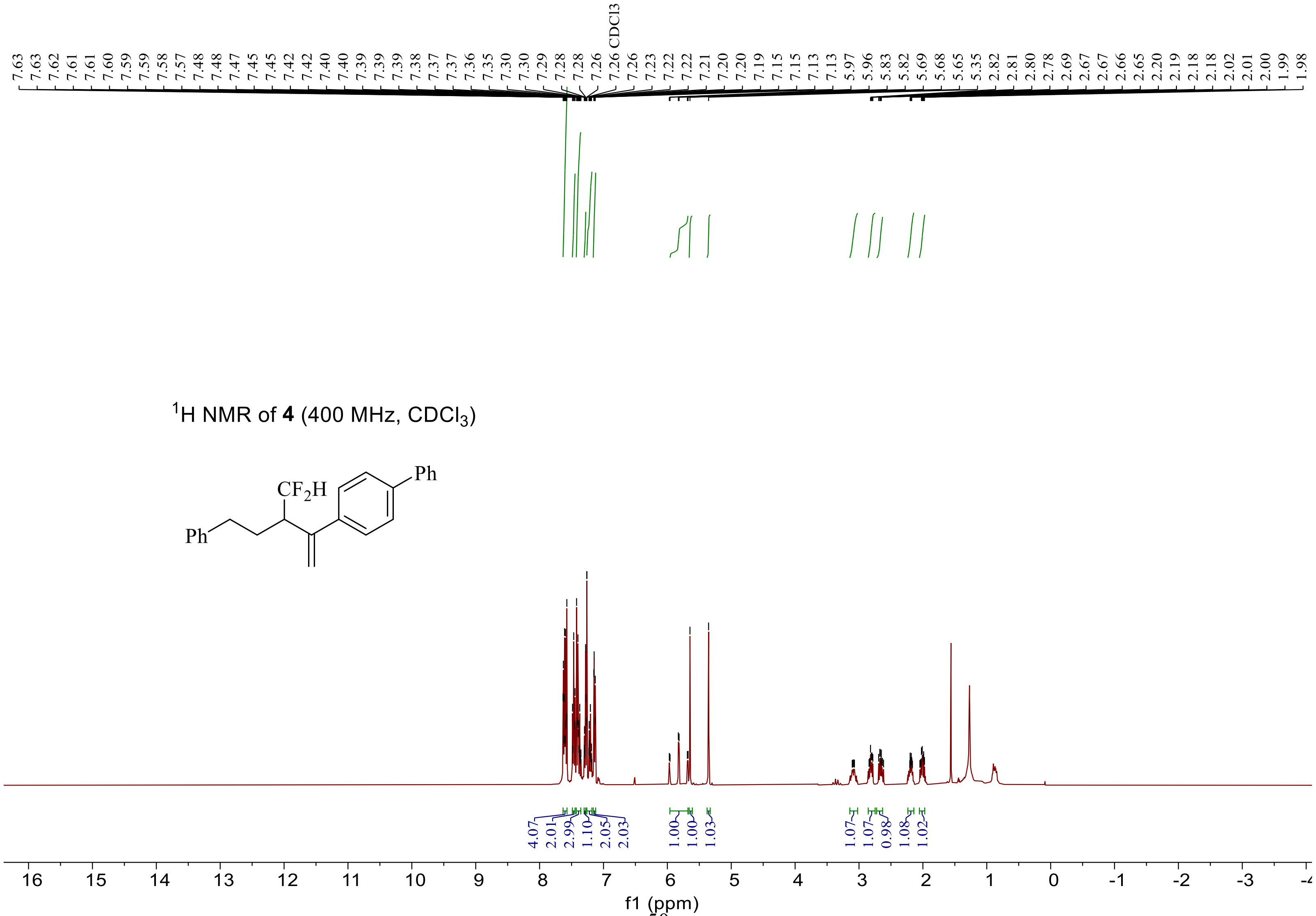




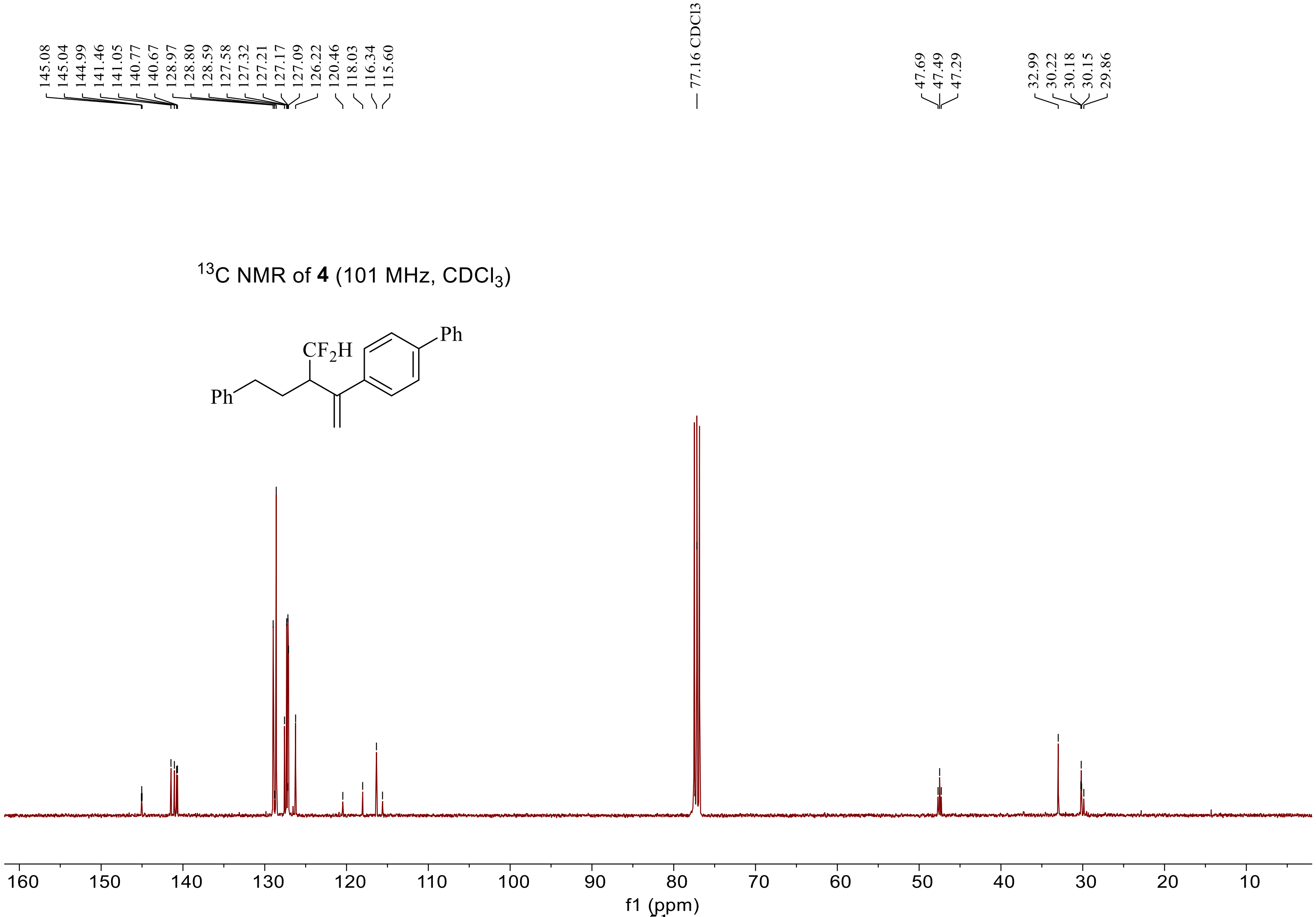
^{13}C NMR of **3** (101 MHz, $CDCl_3$)



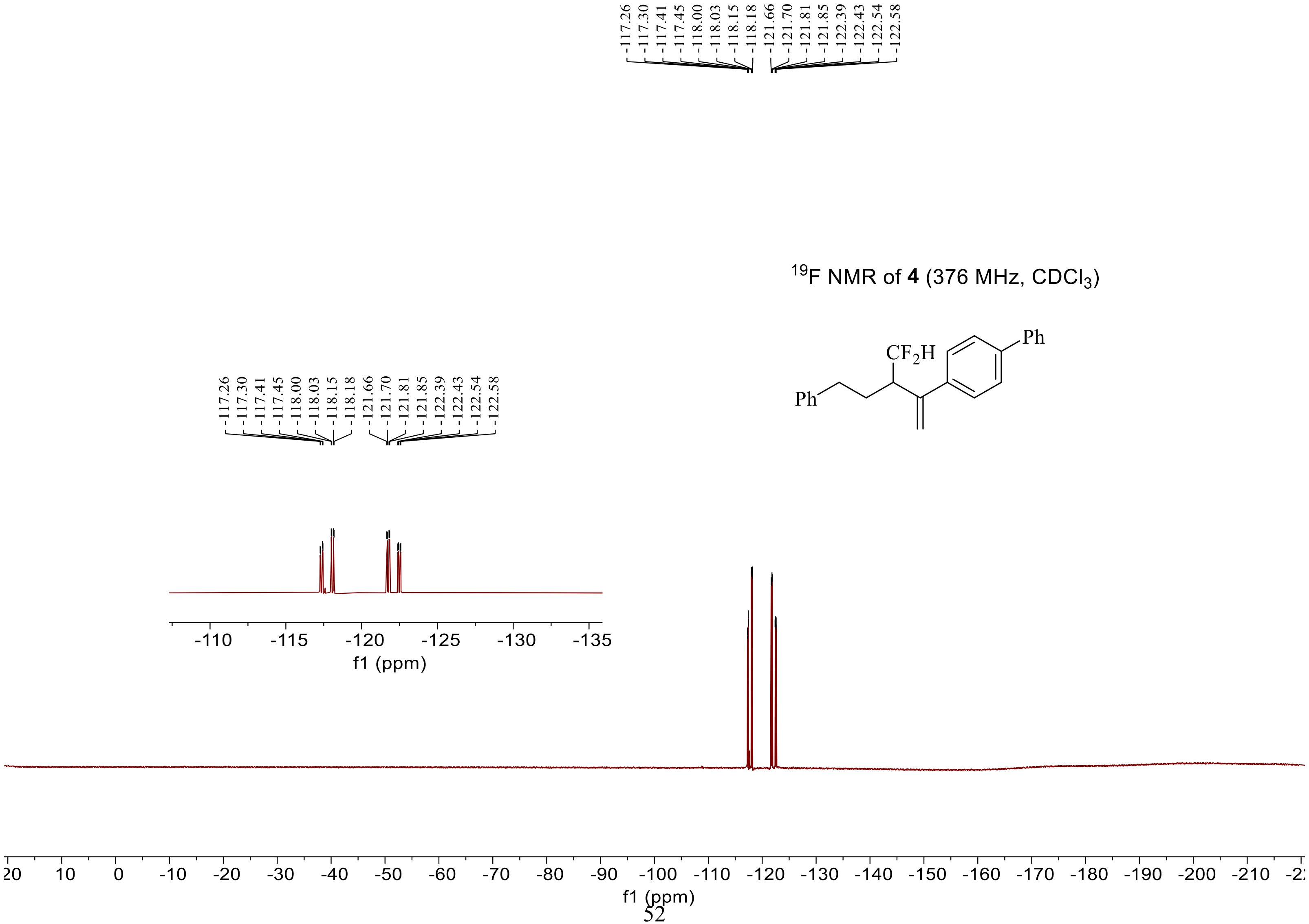
^{19}F NMR of **3** (376 MHz, $CDCl_3$)



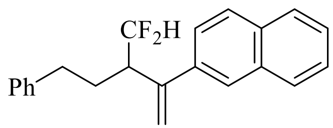
^{1}H NMR of **4** (400 MHz, $CDCl_3$)

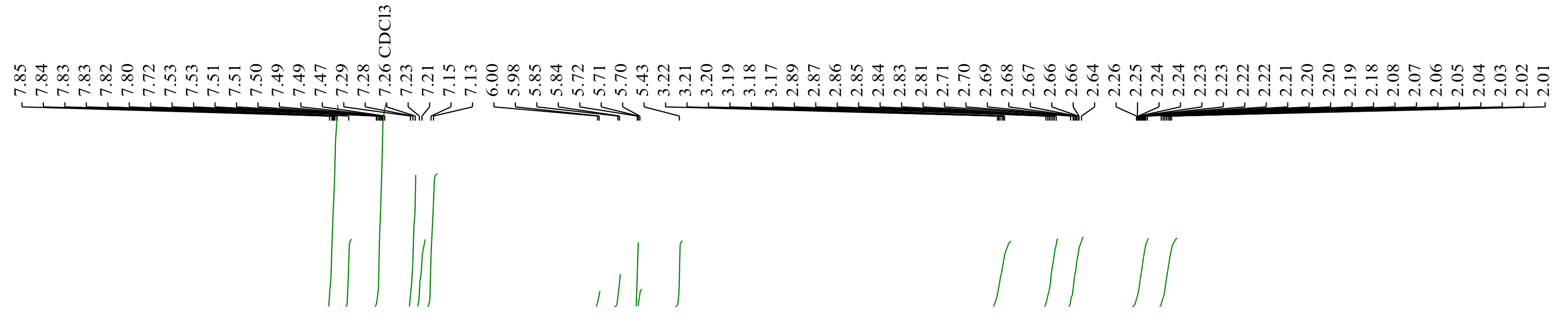

145.08
145.04
144.99
141.46
141.05
140.77
140.67
128.97
128.80
128.59
127.58
127.32
127.21
127.17
127.09
126.22
120.46
118.03
116.34
115.60
77.16 CDCl3
47.69
47.49
47.29
32.99
30.22
30.18
30.15
29.86
^{13}C NMR of **4** (101 MHz, $CDCl_3$)
CF_2H
Ph
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

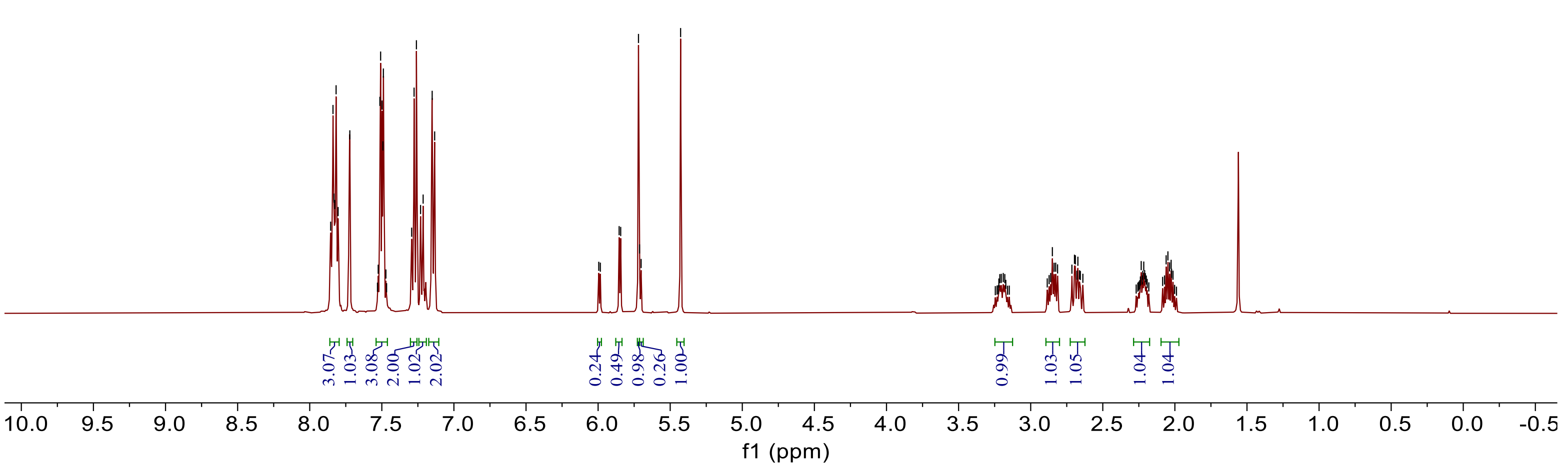
^{19}F NMR of **4** (376 MHz, $CDCl_3$)



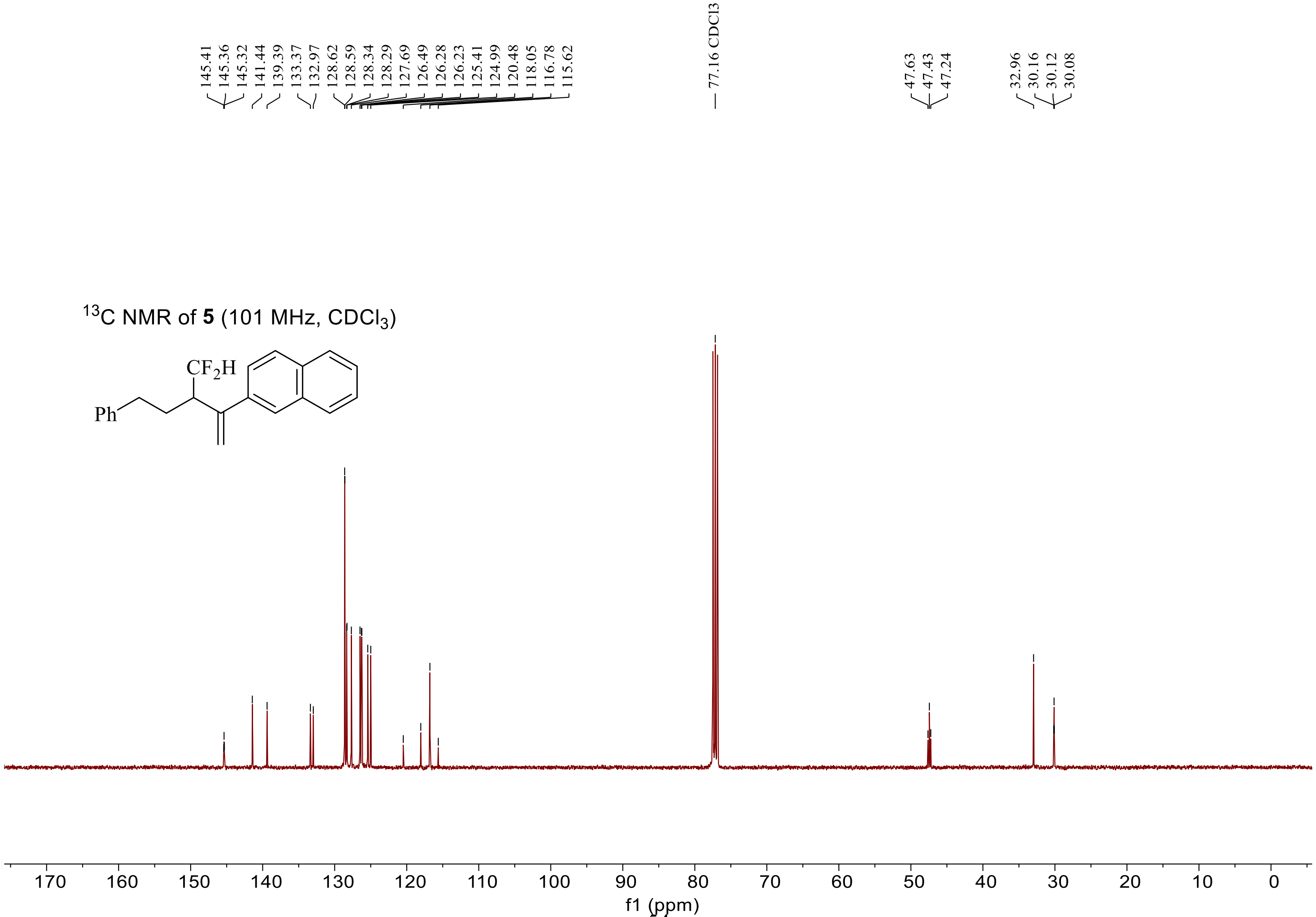
[1]H NMR of **5** (400 MHz, $CDCl_3$)

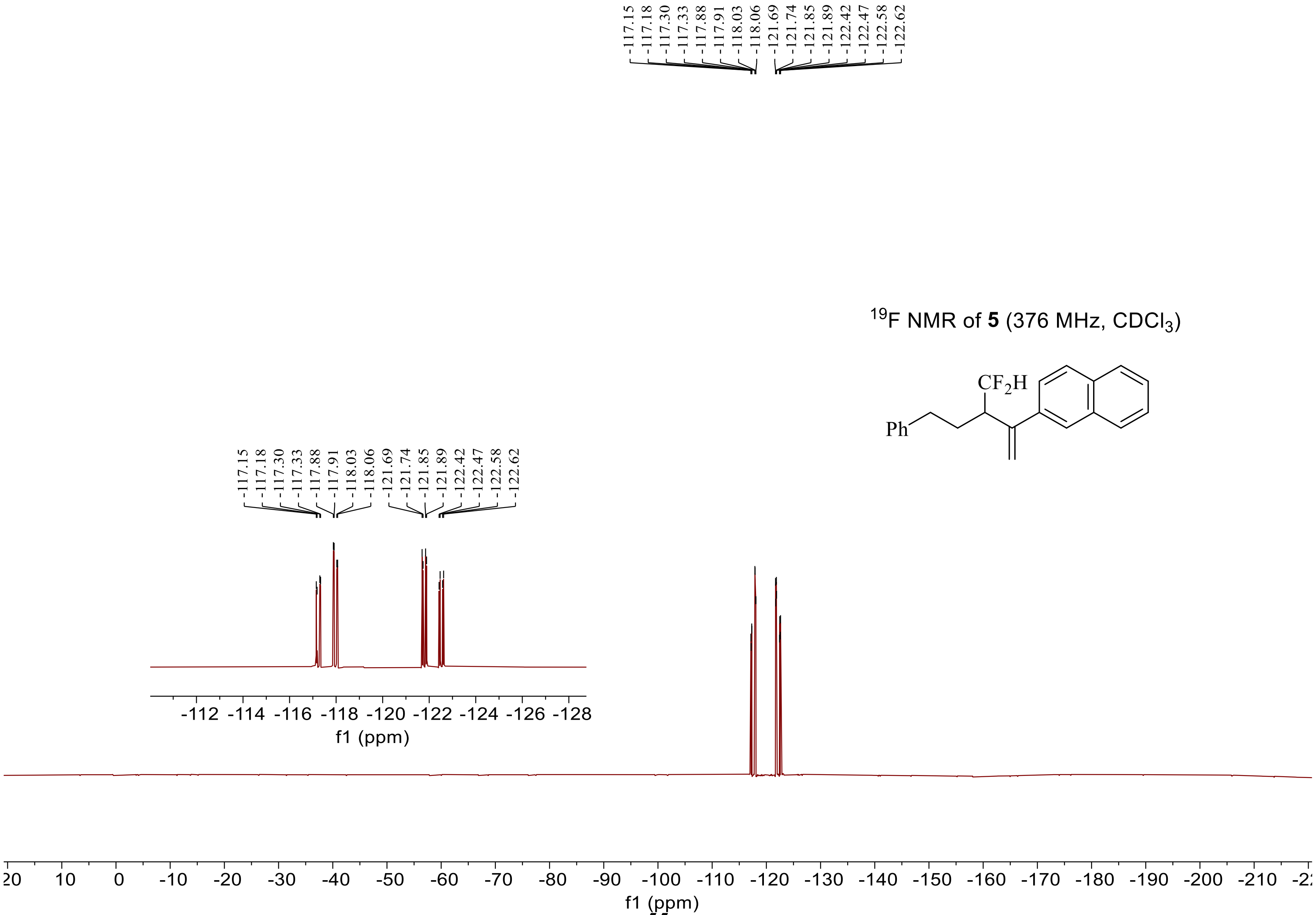




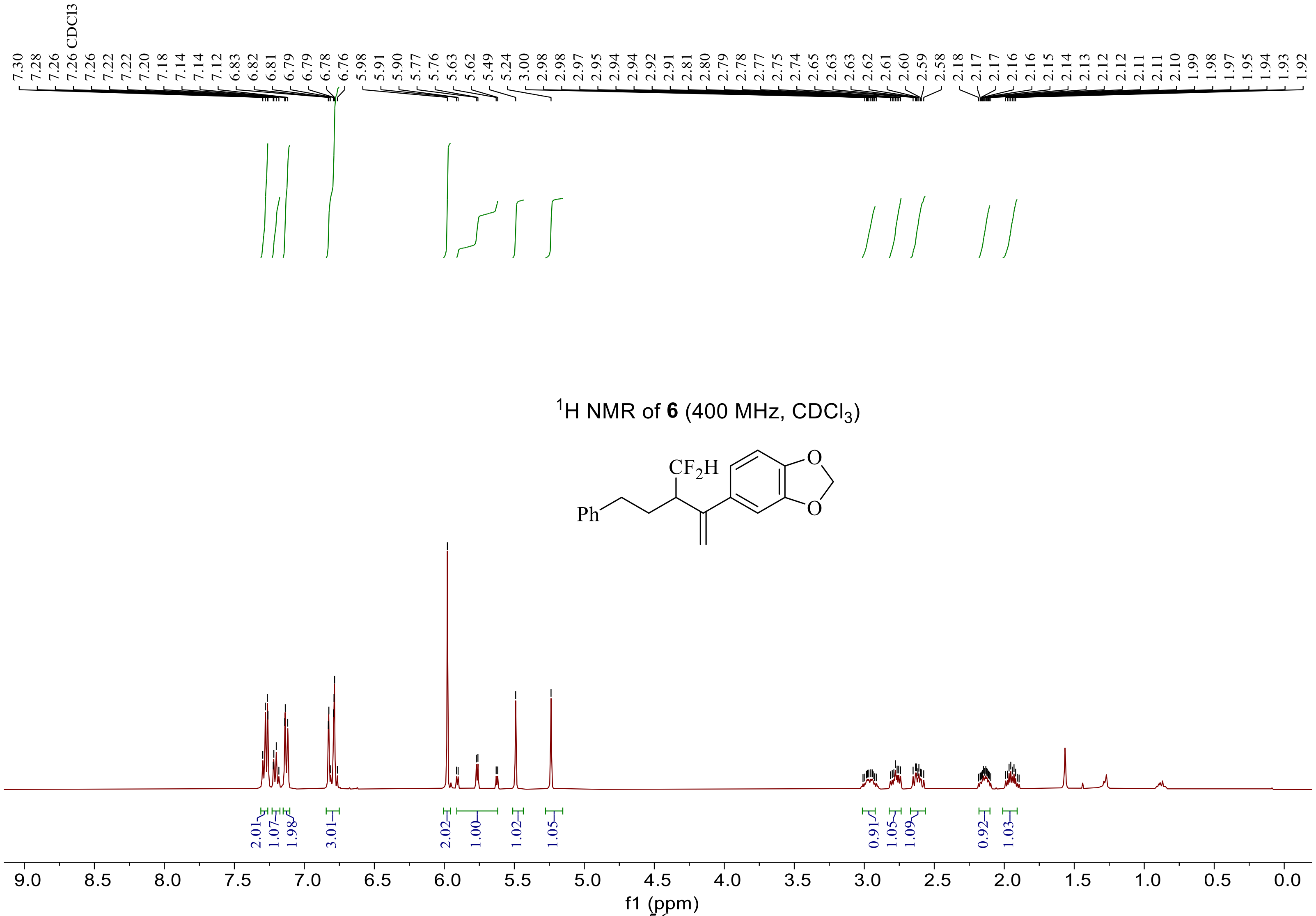


^{13}C NMR of **5** (101 MHz, $CDCl_3$)



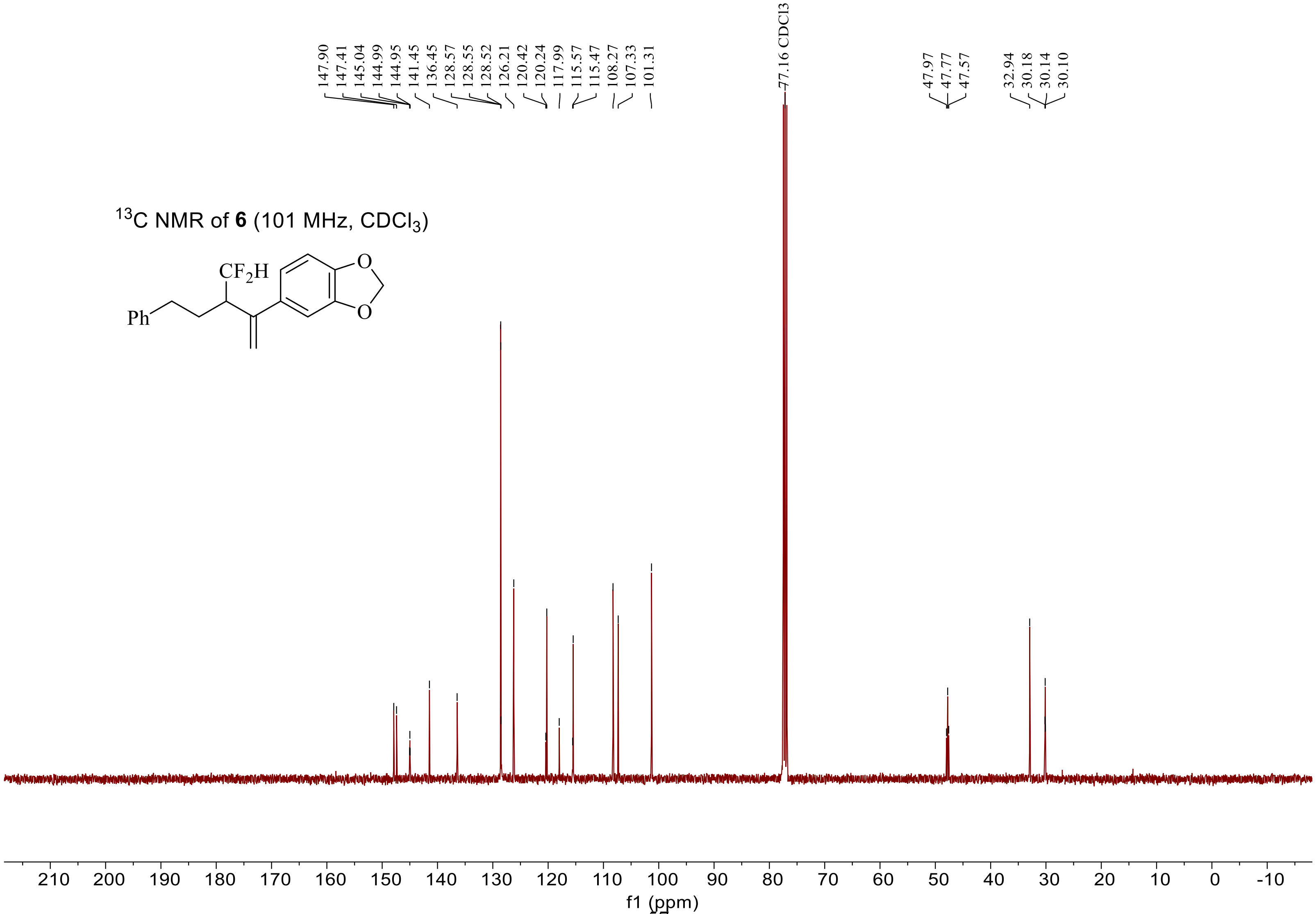


^{19}F NMR of **5** (376 MHz, $CDCl_3$)

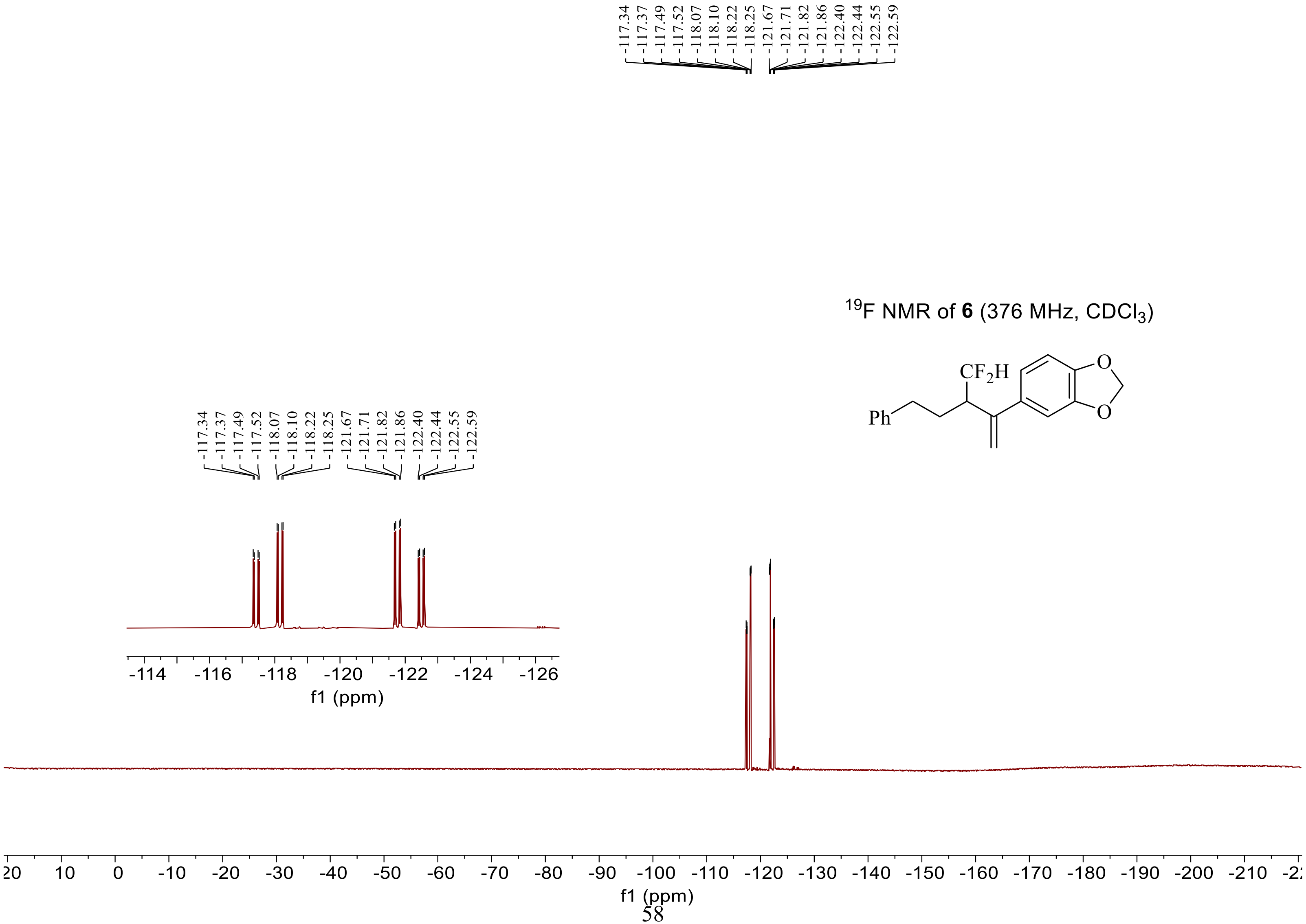


^{1}H NMR of **6** (400 MHz, $CDCl_3$)

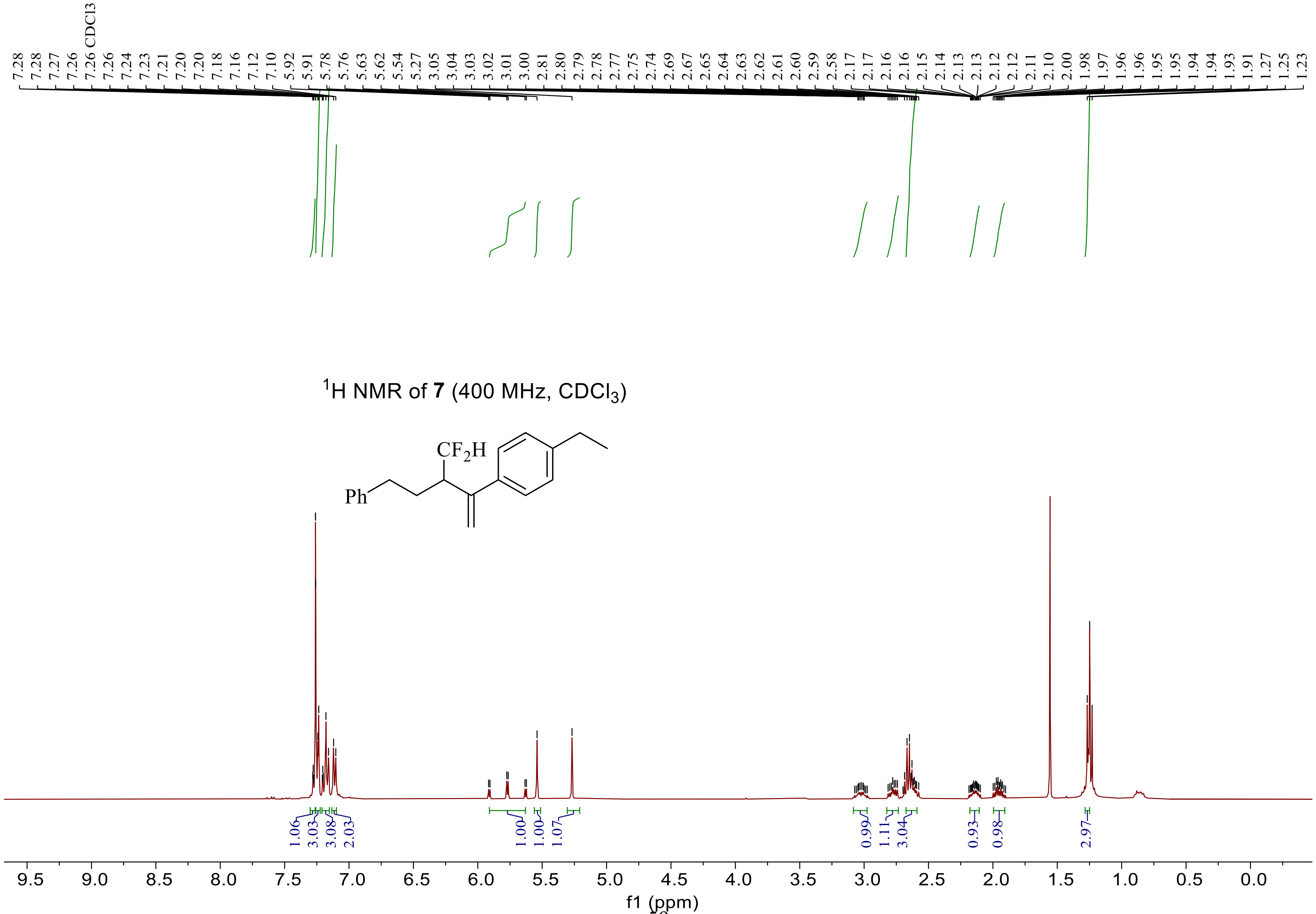
^{13}C NMR of **6** (101 MHz, $CDCl_3$)

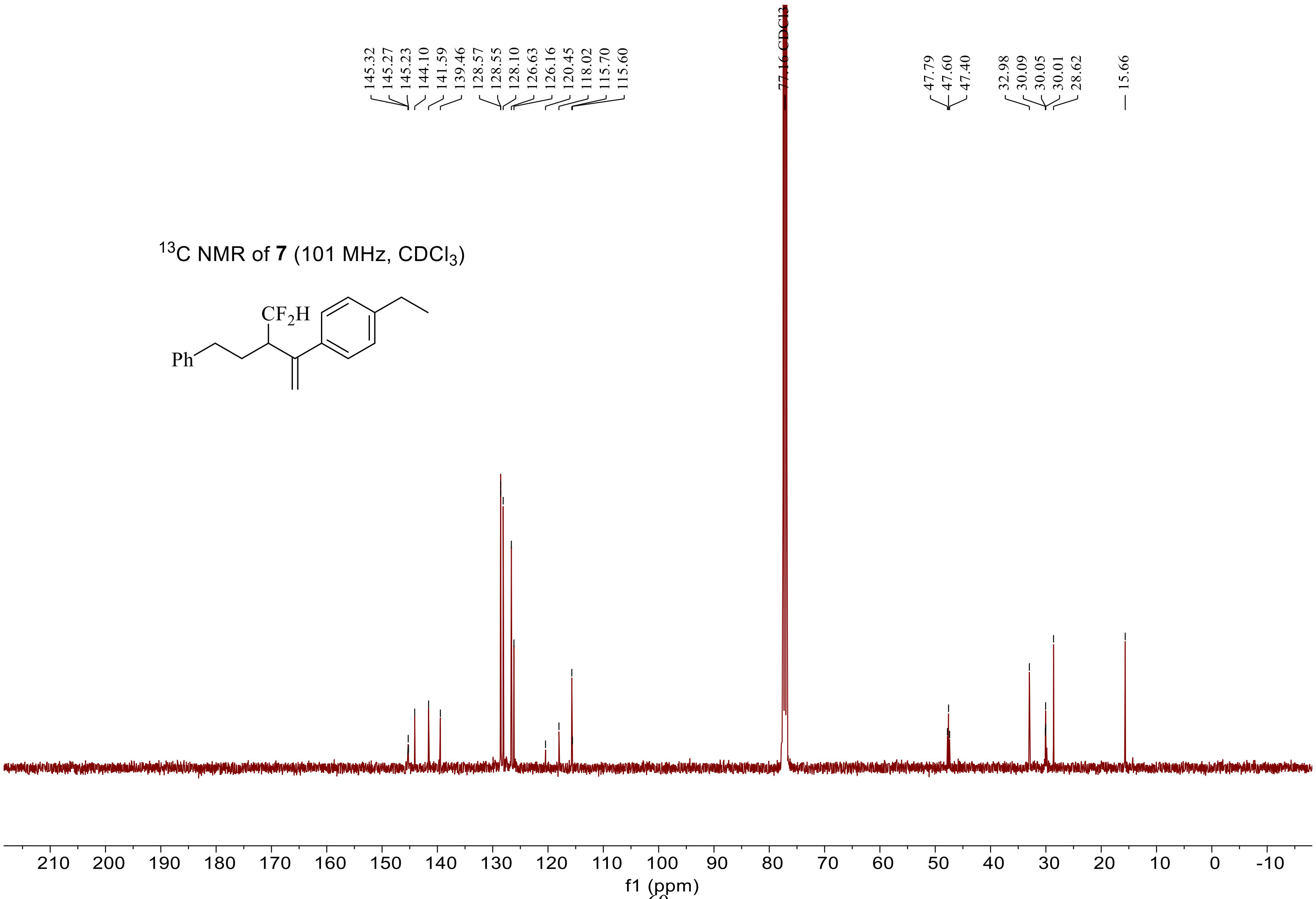


^{19}F NMR of **6** (376 MHz, $CDCl_3$)



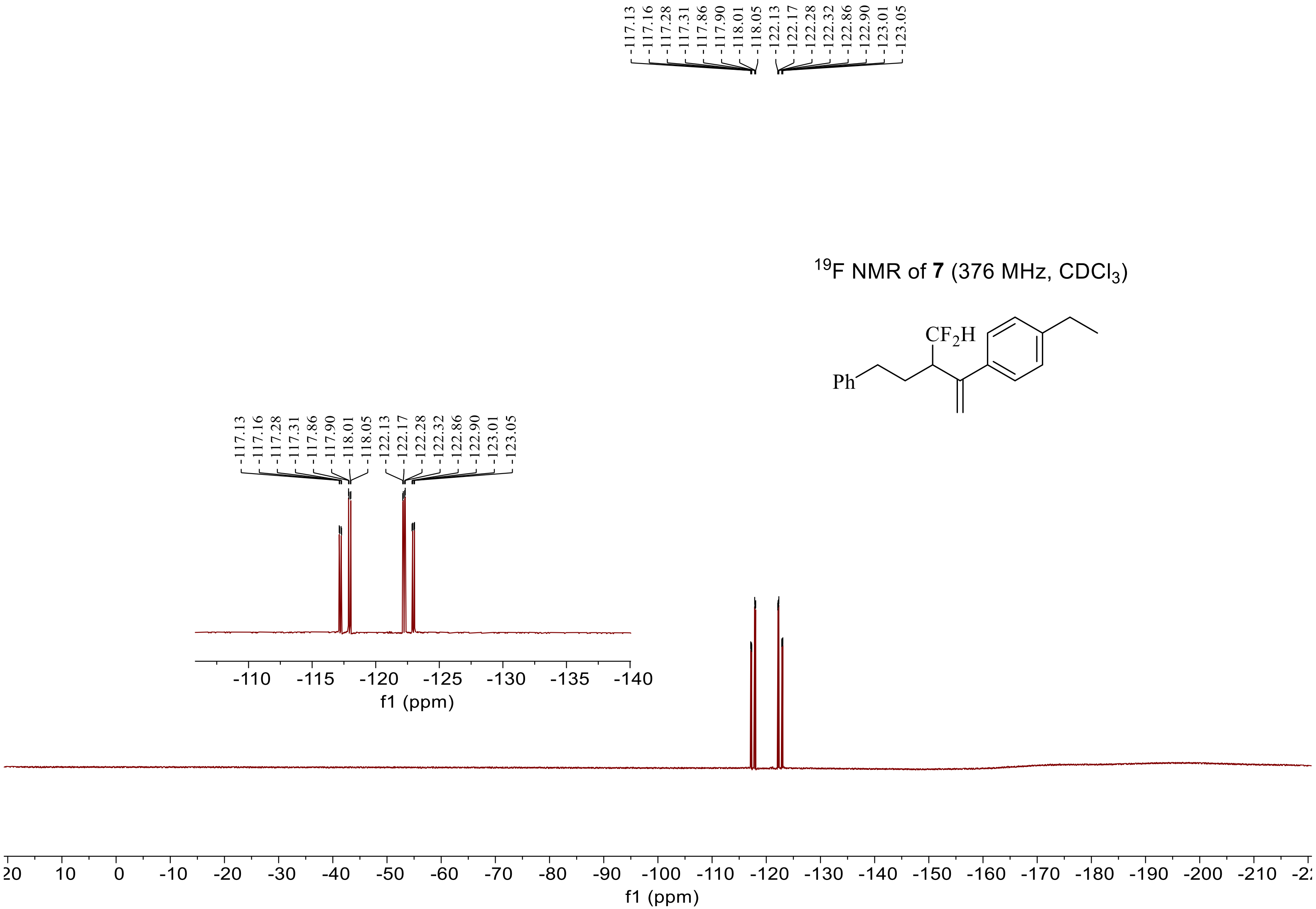
[1]H NMR of **7** (400 MHz, $CDCl_3$)



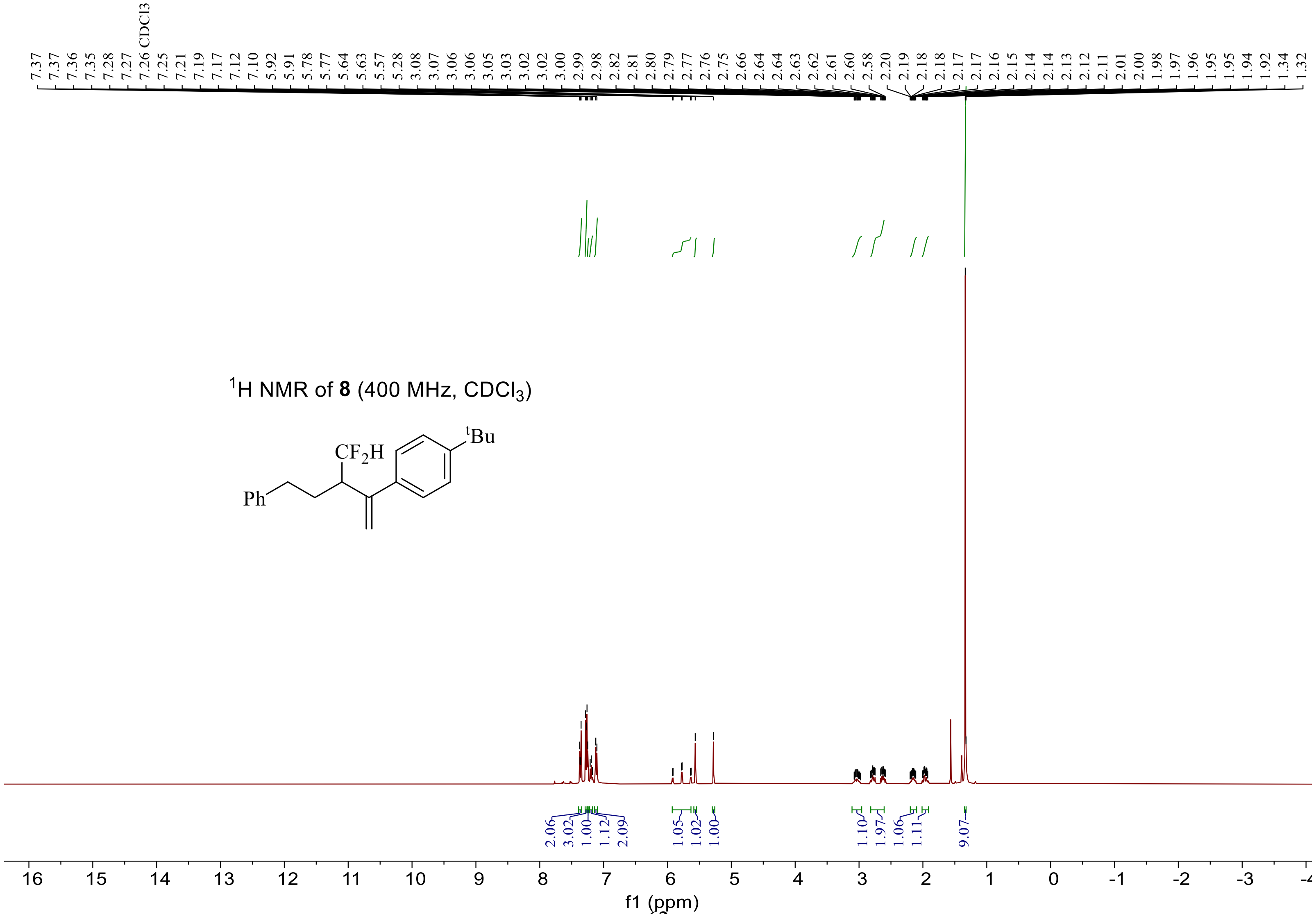


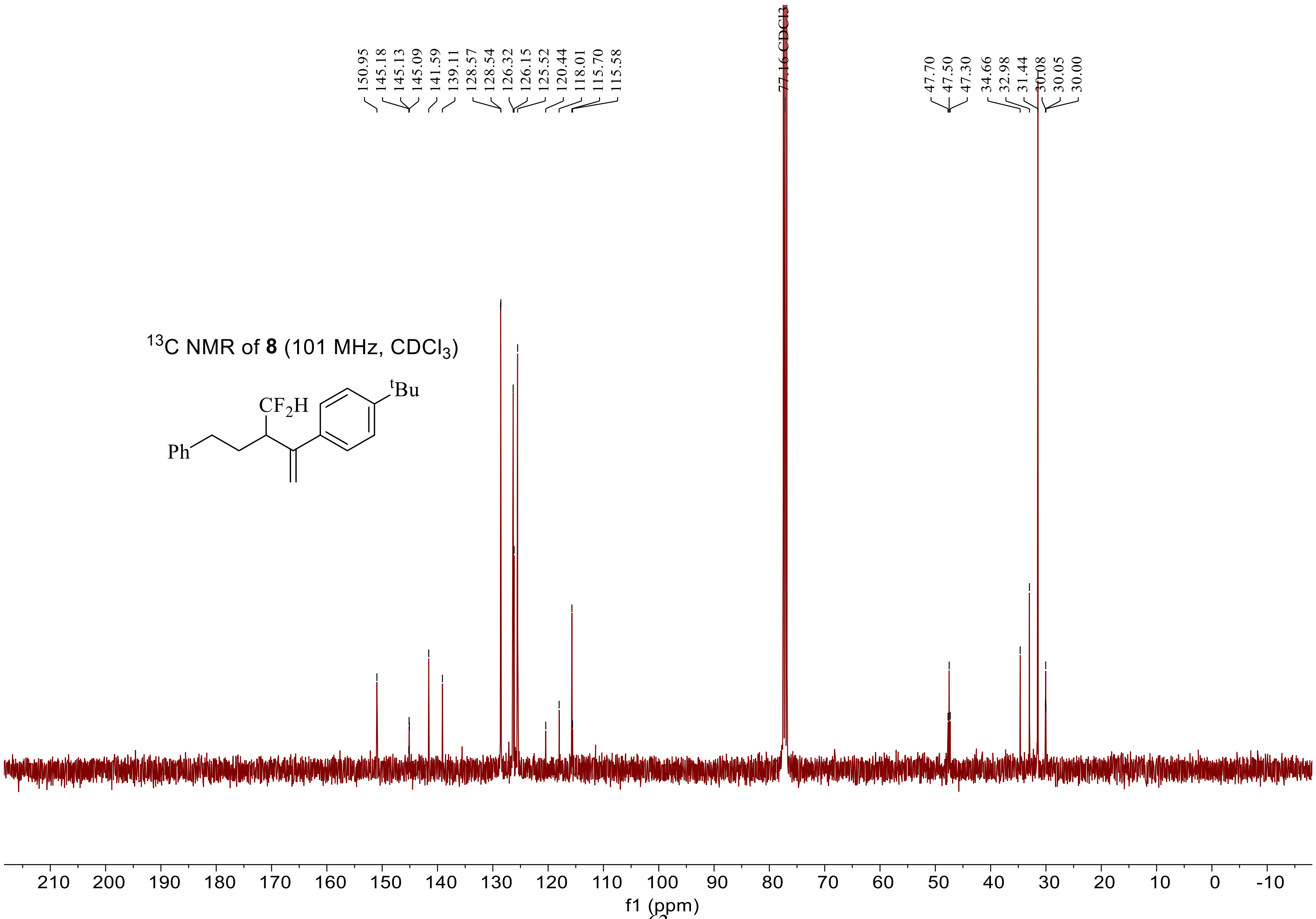
13C NMR of 7 (101 MHz, CDCl3)
CF2H
Ph
145.32
145.27
145.23
144.10
141.59
139.46
128.57
128.55
128.10
126.63
126.16
120.45
118.02
115.70
115.60
77.16 CDCl3
47.79
47.60
47.40
32.98
30.09
30.05
30.01
28.62
15.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

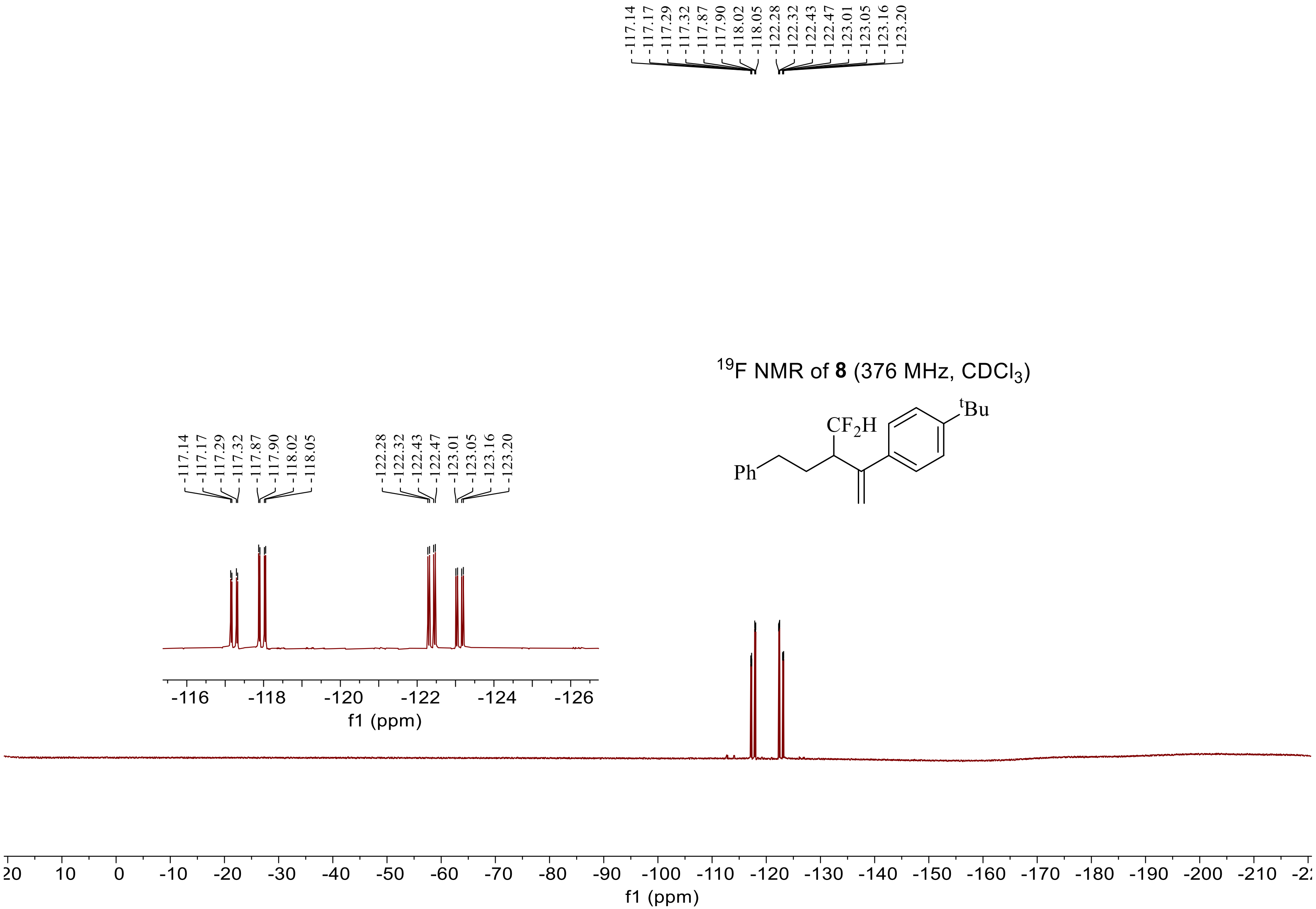
^{19}F NMR of **7** (376 MHz, $CDCl_3$)

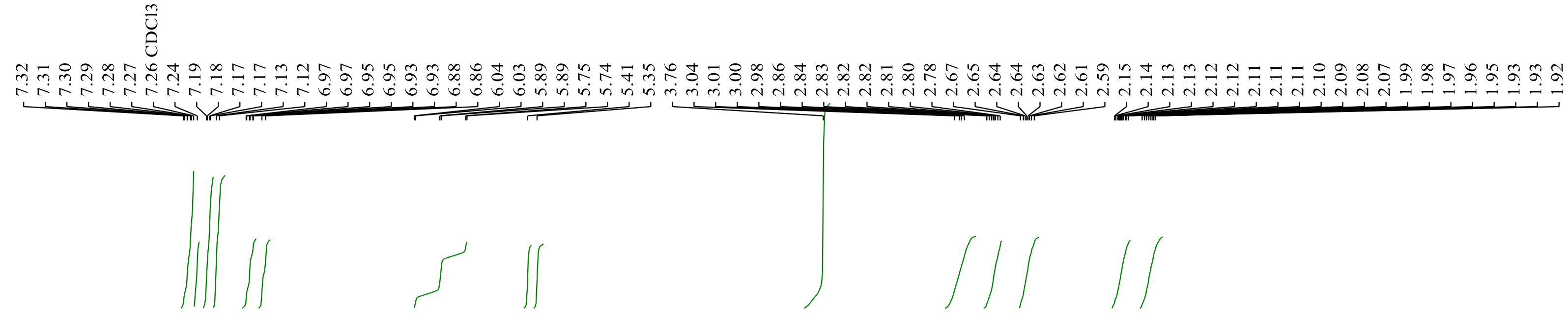


^{1}H NMR of **8** (400 MHz, $CDCl_3$)

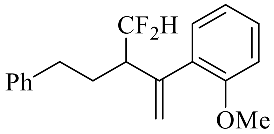


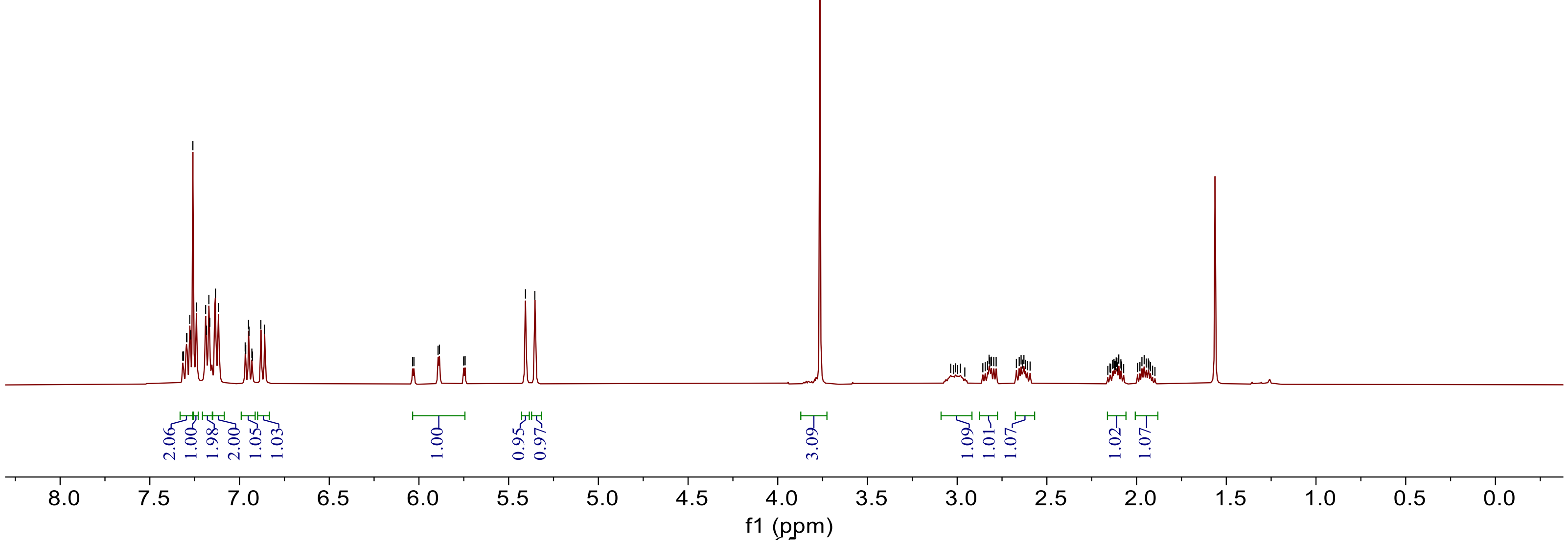

^{13}C NMR of **8** (101 MHz, $CDCl_3$)
CF_2H
^{t}Bu
Ph
150.95
145.18
145.13
145.09
141.59
139.11
128.57
128.54
126.32
126.15
125.52
120.44
118.01
115.70
115.58
77.16 CDCl3
47.70
47.50
47.30
34.66
32.98
31.44
30.08
30.05
30.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

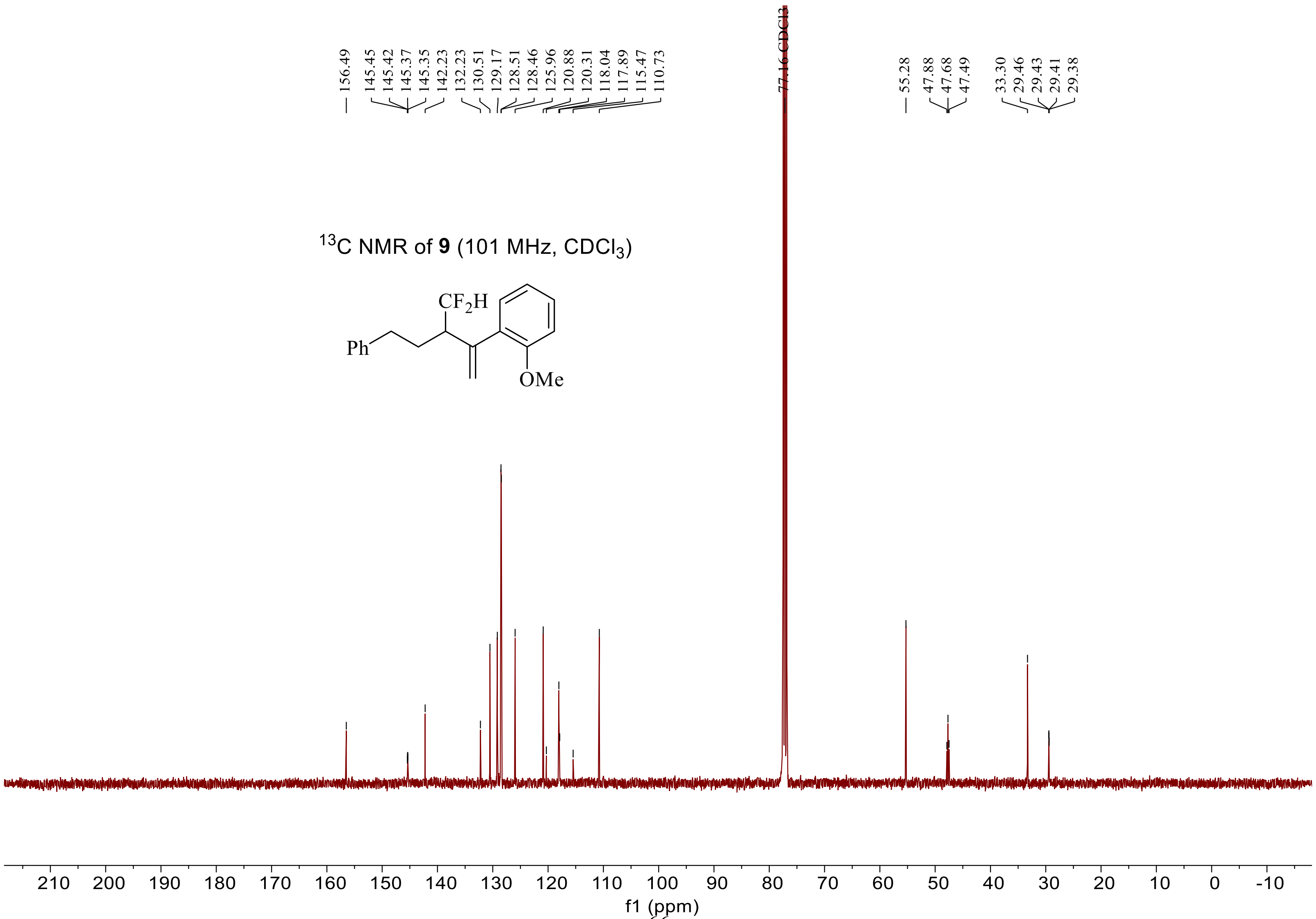

-117.14
-117.17
-117.29
-117.32
-117.87
-117.90
-118.02
-118.05
-122.28
-122.32
-122.43
-122.47
-123.01
-123.05
-123.16
-123.20
^{19}F NMR of **8** (376 MHz, $CDCl_3$)
CF_2H
^{t}Bu
Ph
f1 (ppm)

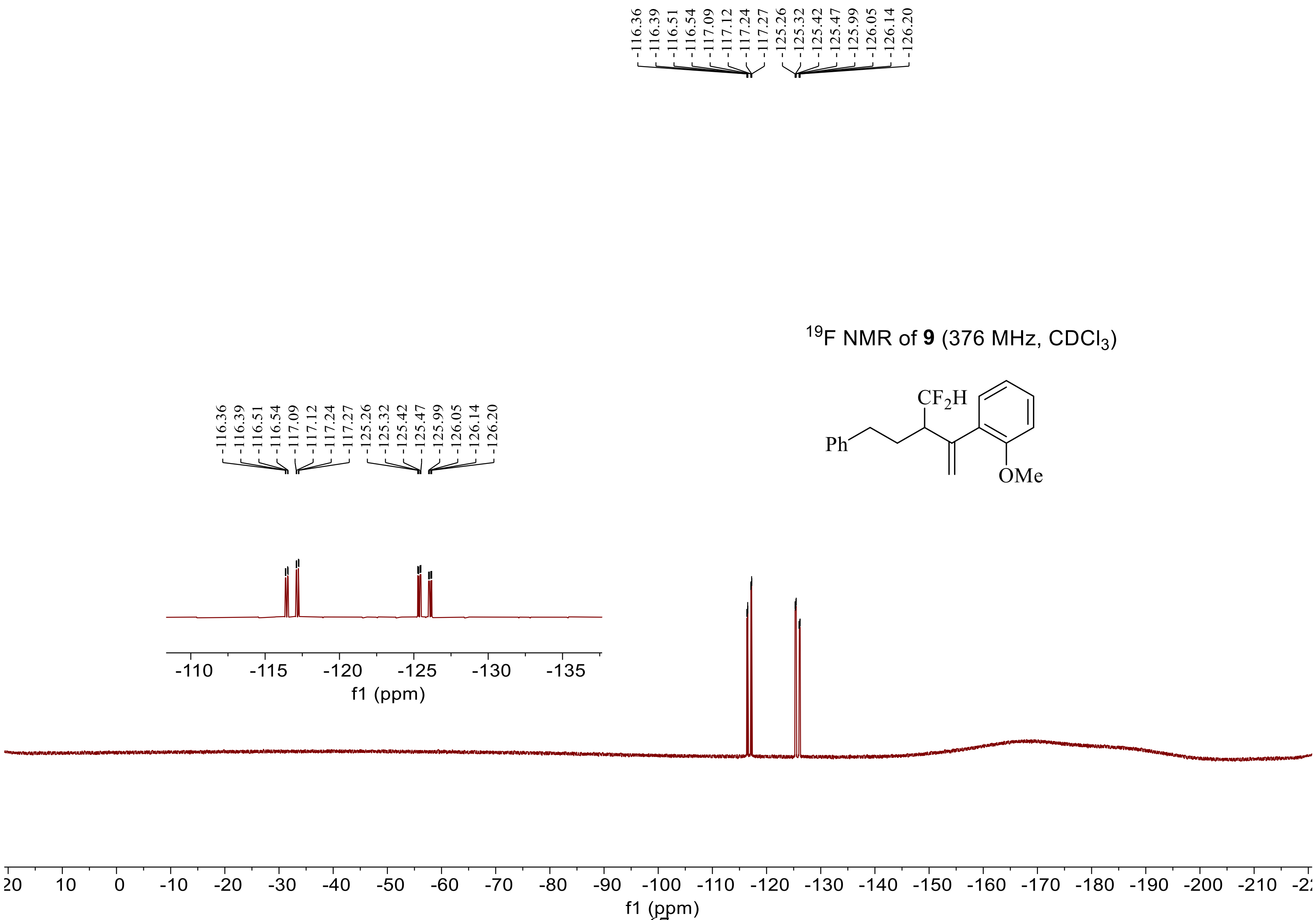


^1H NMR of **9** (400 MHz, $CDCl_3$)

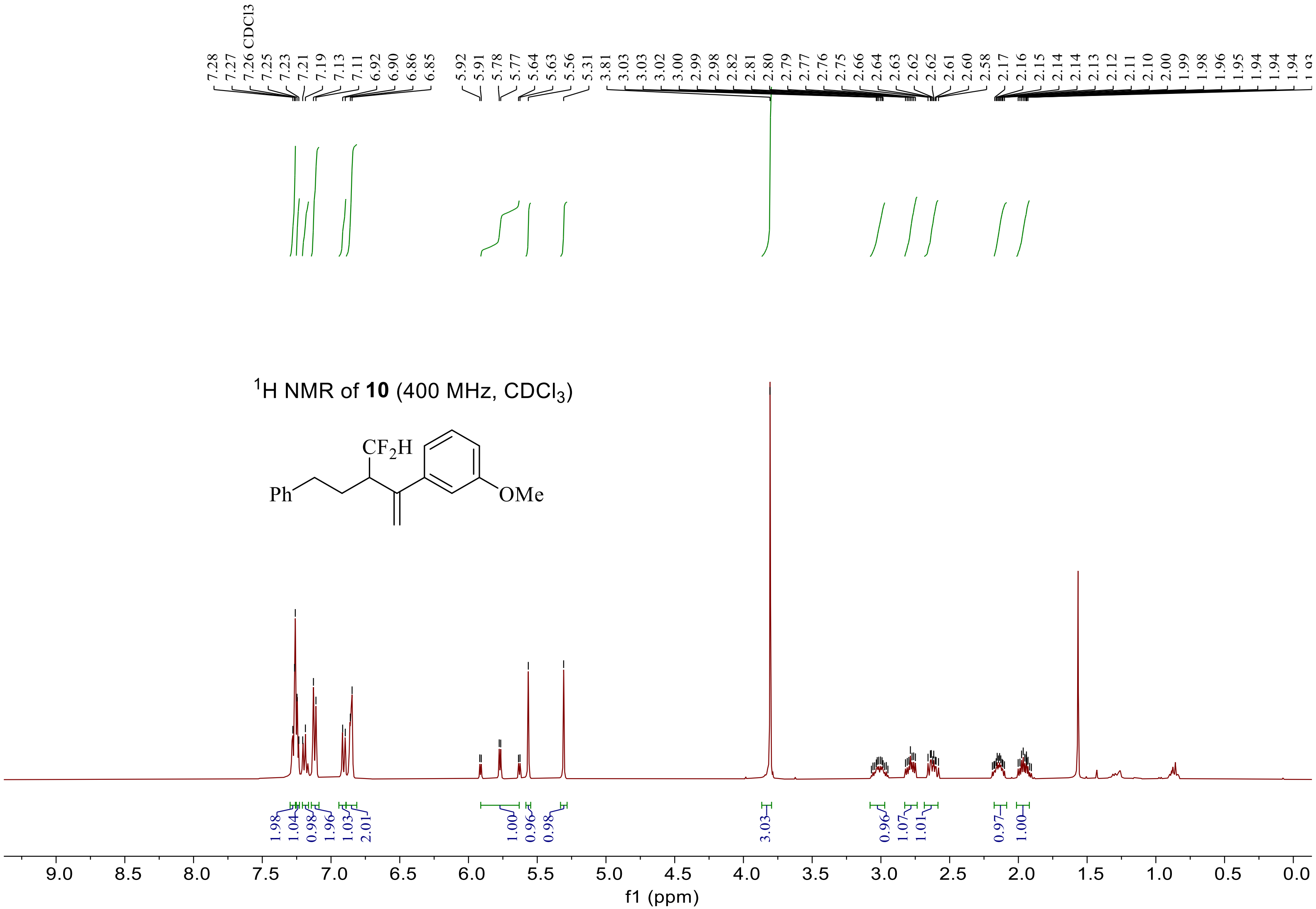




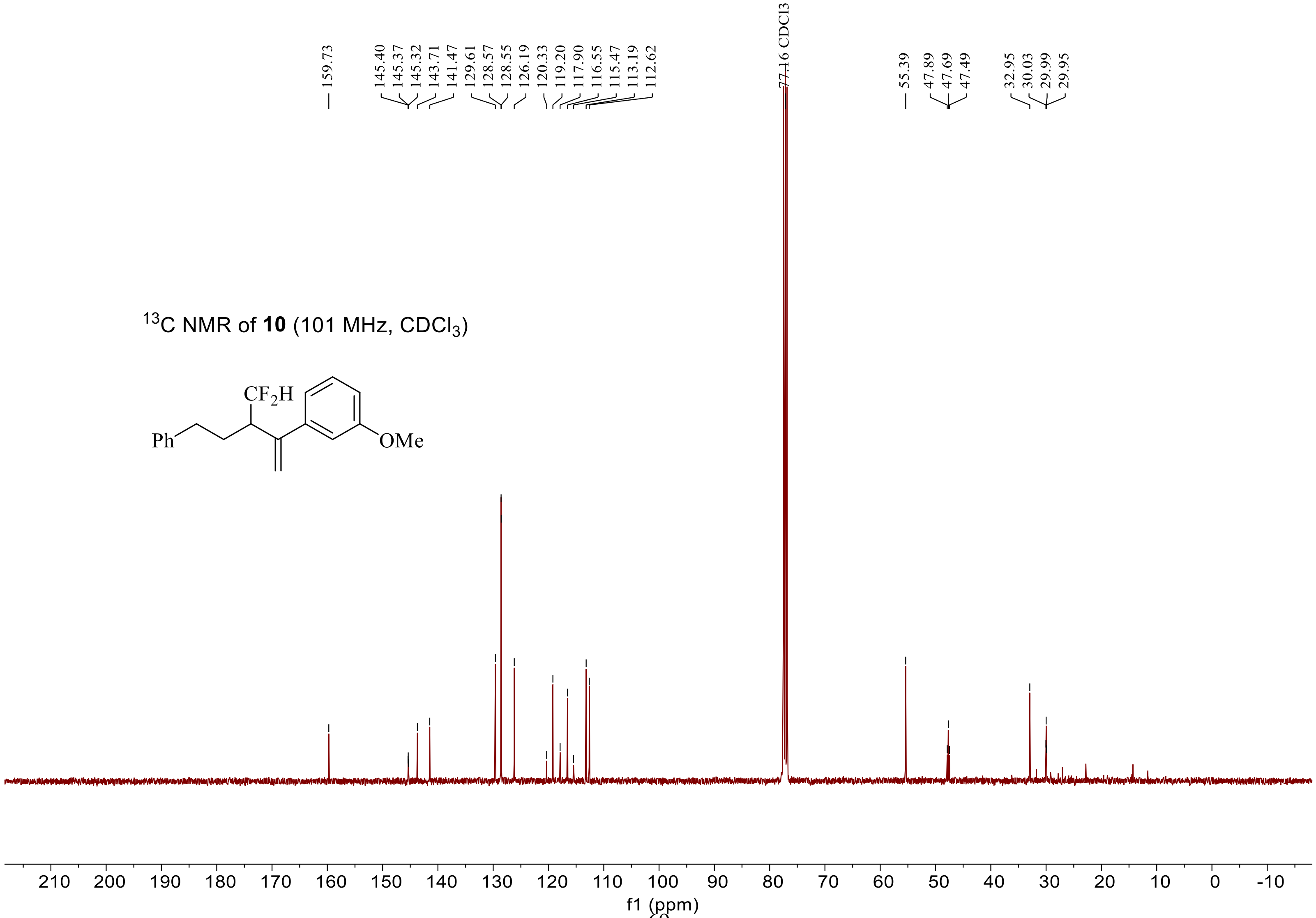

156.49
145.45
145.42
145.37
145.35
142.23
132.23
130.51
129.17
128.51
128.46
125.96
120.88
120.31
118.04
117.89
115.47
110.73
77.16 CDCl3
55.28
47.88
47.68
47.49
33.30
29.46
29.43
29.41
29.38
^{13}C NMR of **9** (101 MHz, $CDCl_3$)
CF_2H
Ph
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



^{19}F NMR of **9** (376 MHz, $CDCl_3$)

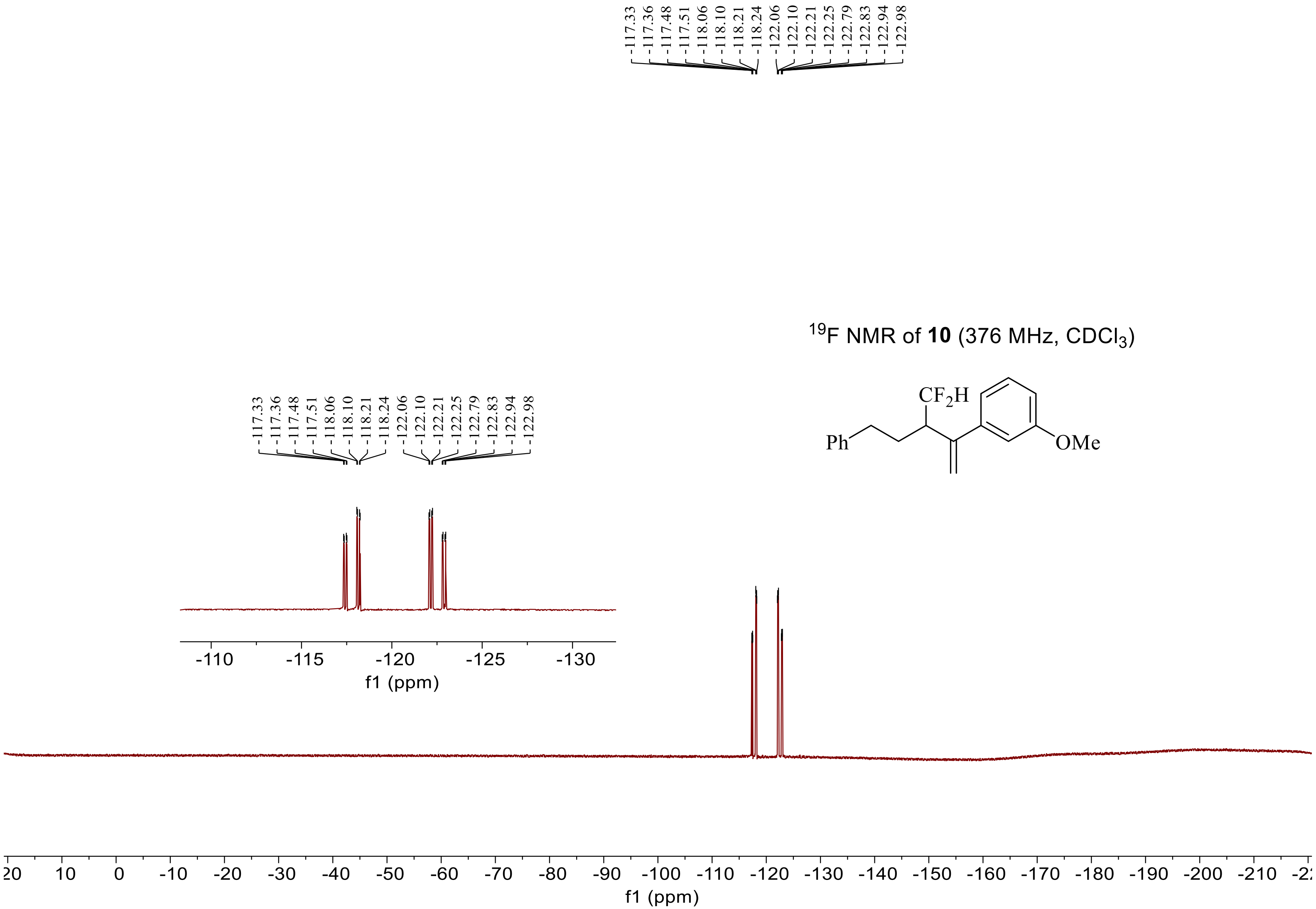


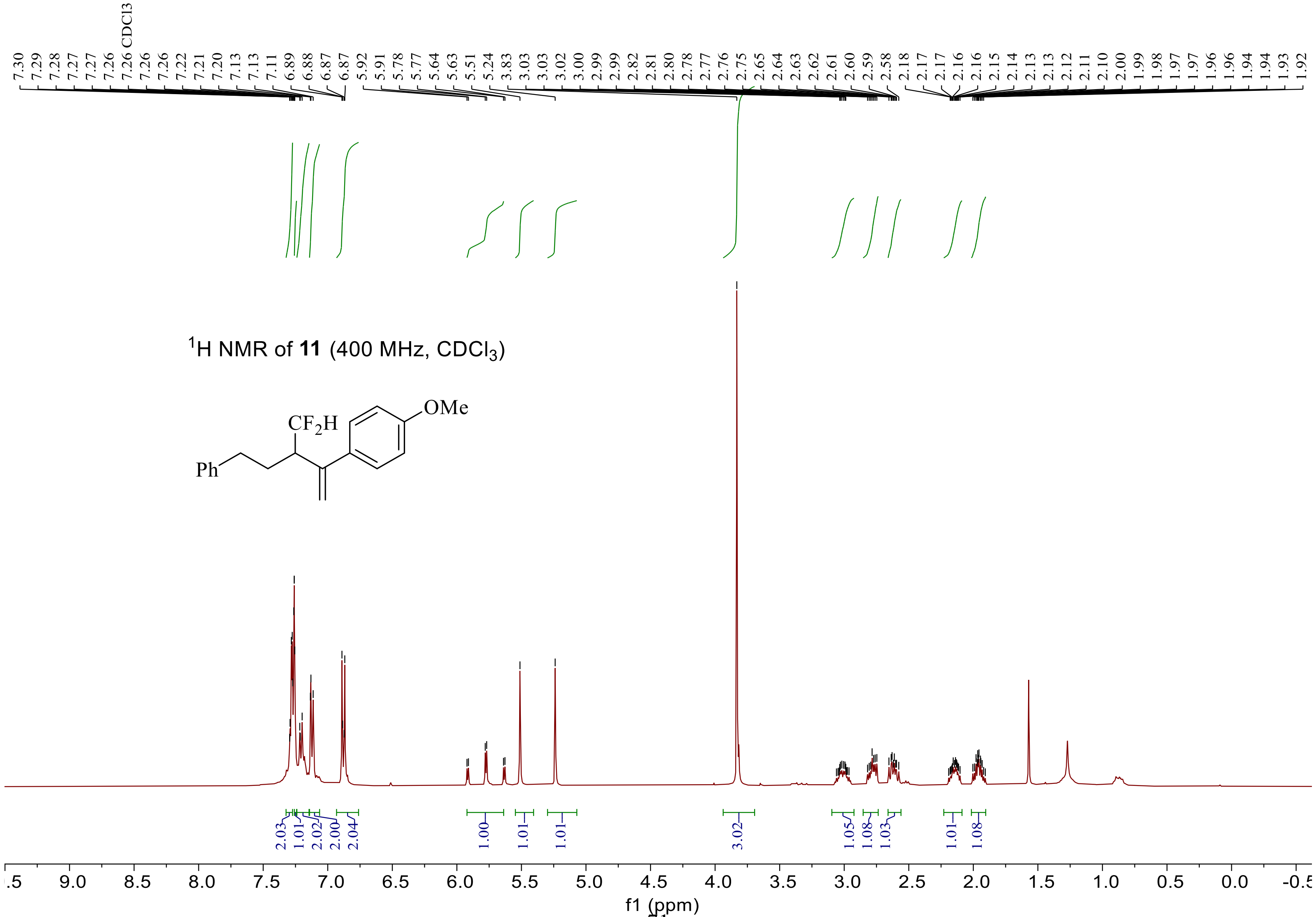
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



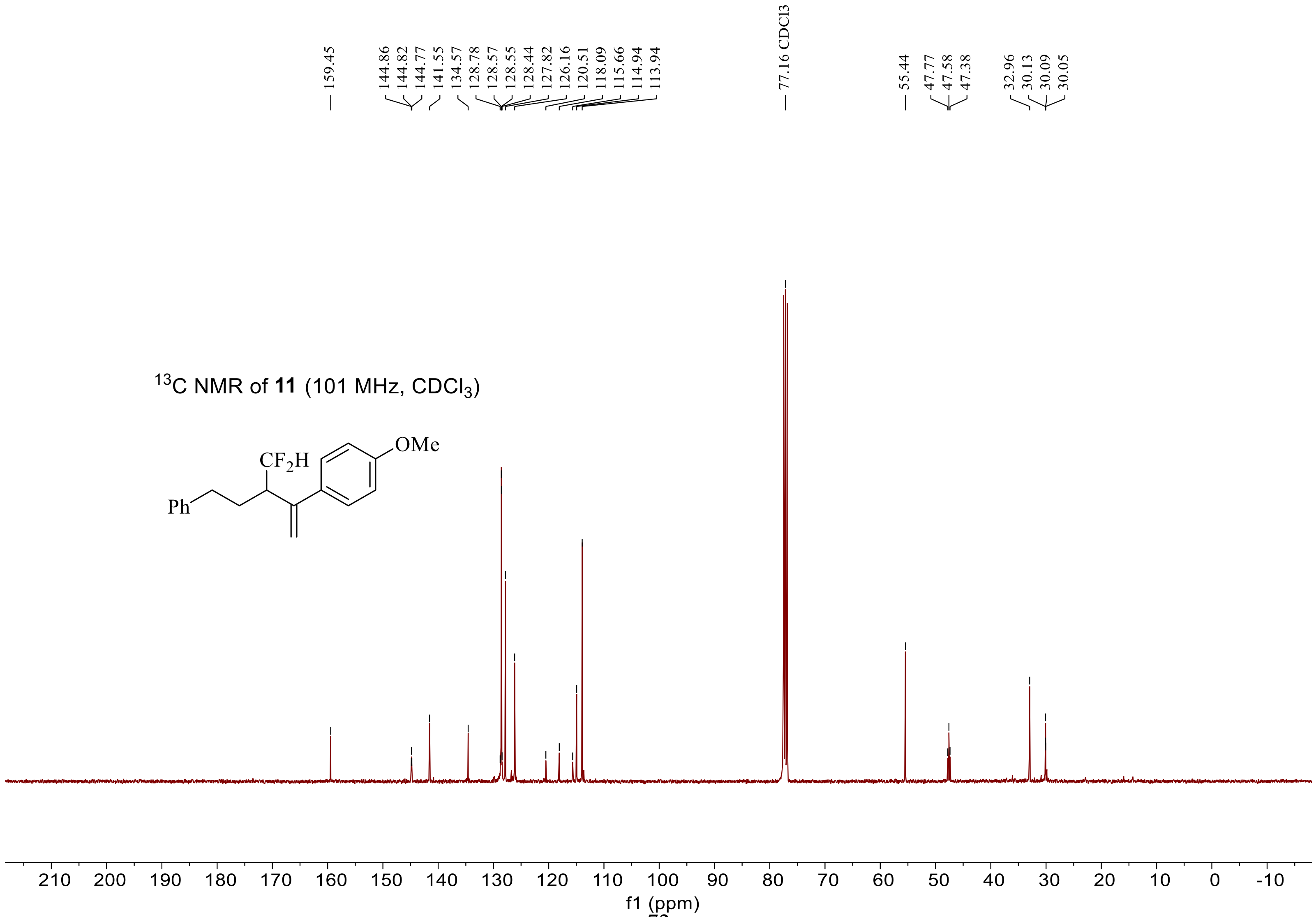
159.73
145.40
145.37
145.32
143.71
141.47
129.61
128.57
128.55
126.19
120.33
119.20
117.90
116.55
115.47
113.19
112.62
77.16 CDCl3
55.39
47.89
47.69
47.49
32.95
30.03
29.99
29.95
^{13}C NMR of **10** (101 MHz, $CDCl_3$)
CF_2H
Ph
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR of **10** (376 MHz, $CDCl_3$)



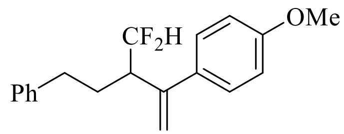


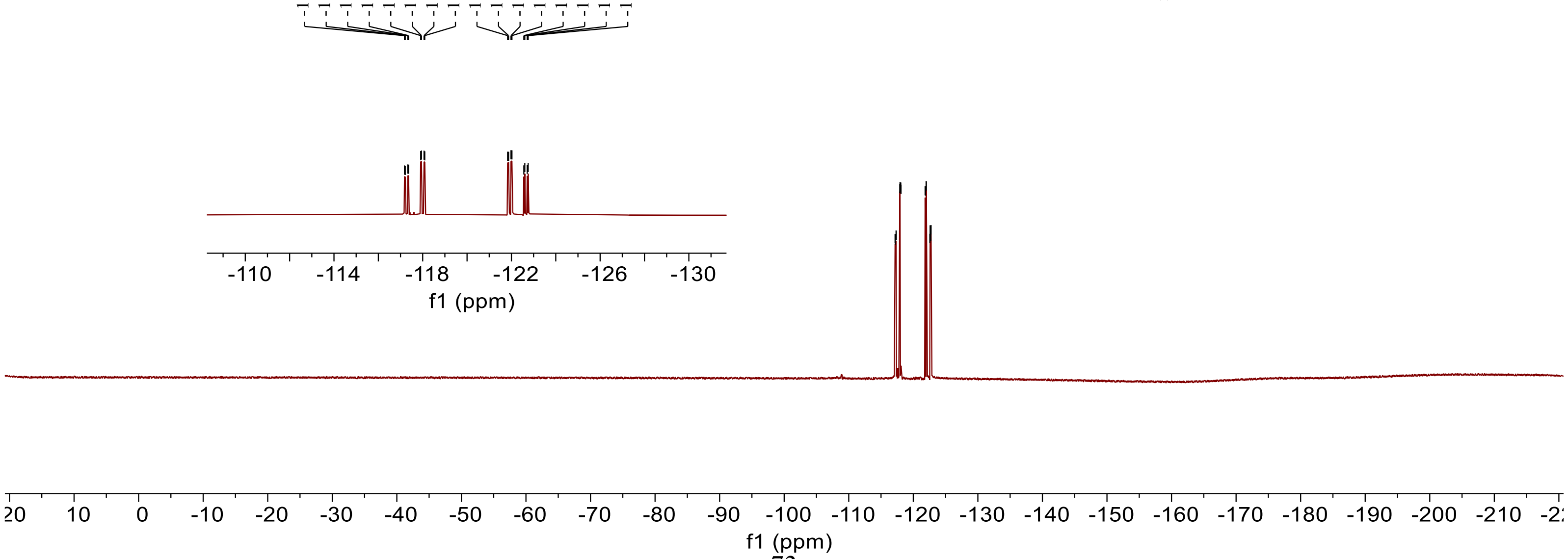
[1]H NMR of **11** (400 MHz, CDCl3)
CF2H
OMe
Ph
f1 (ppm)

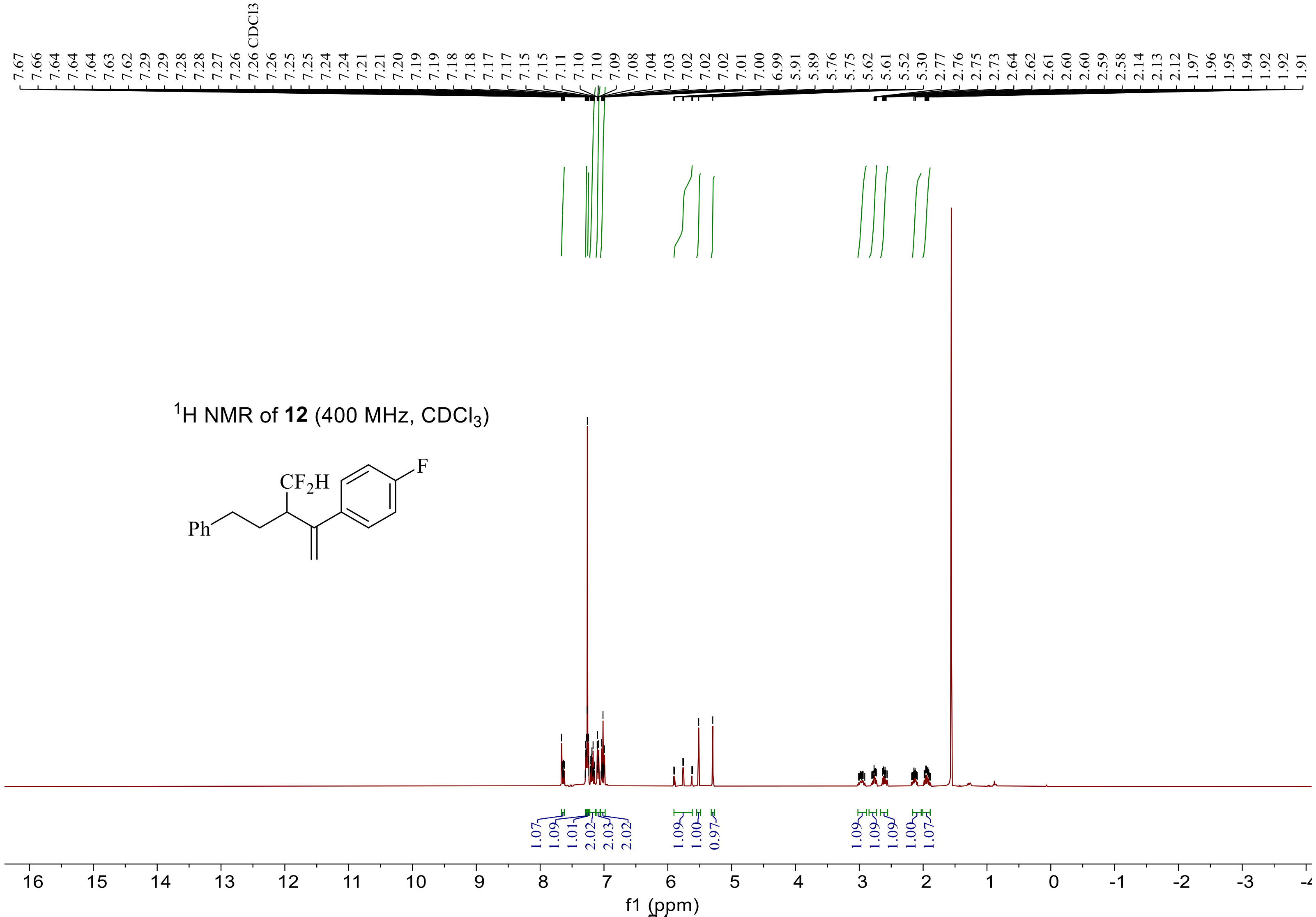


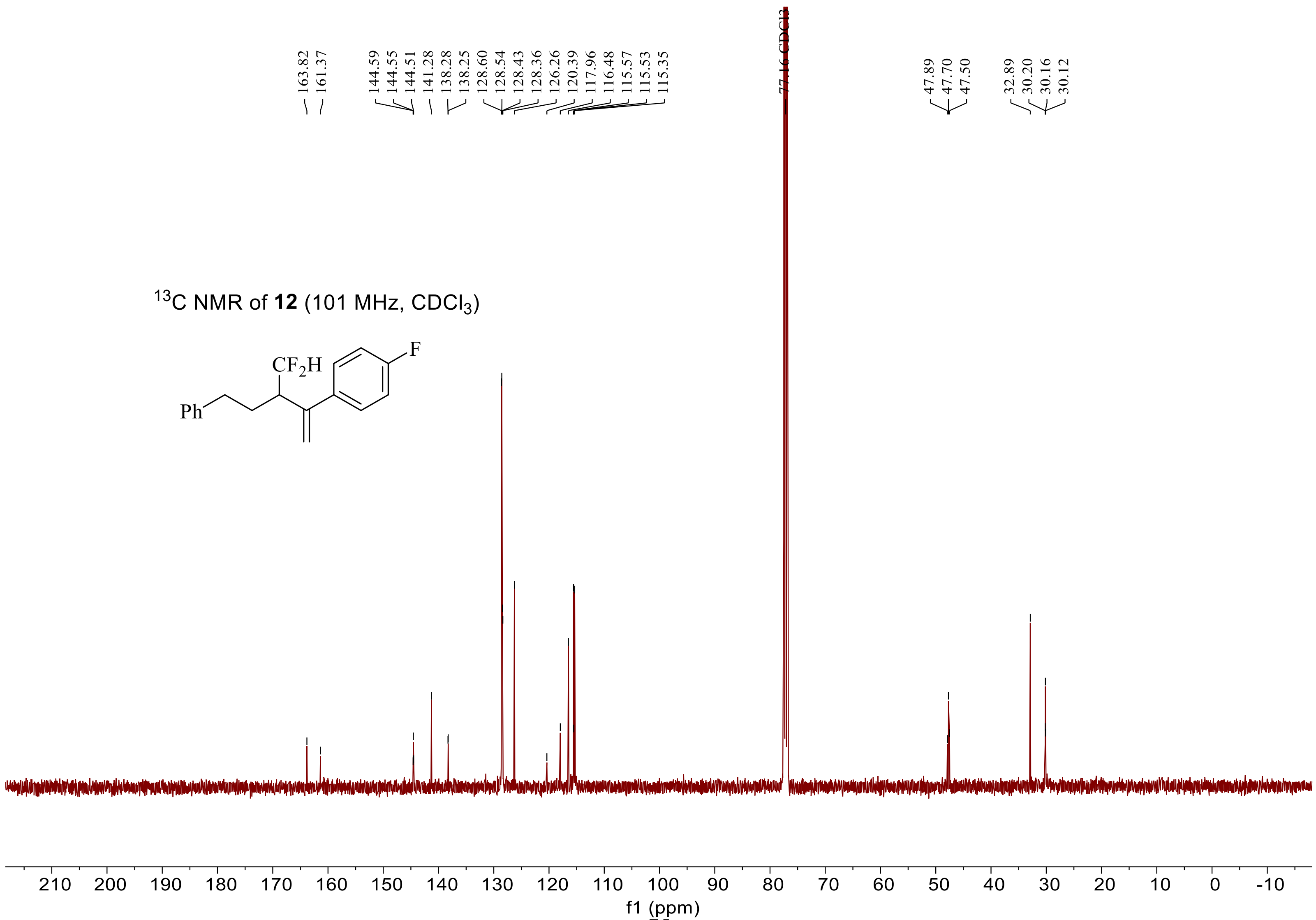
^{13}C NMR of **11** (101 MHz, $CDCl_3$)

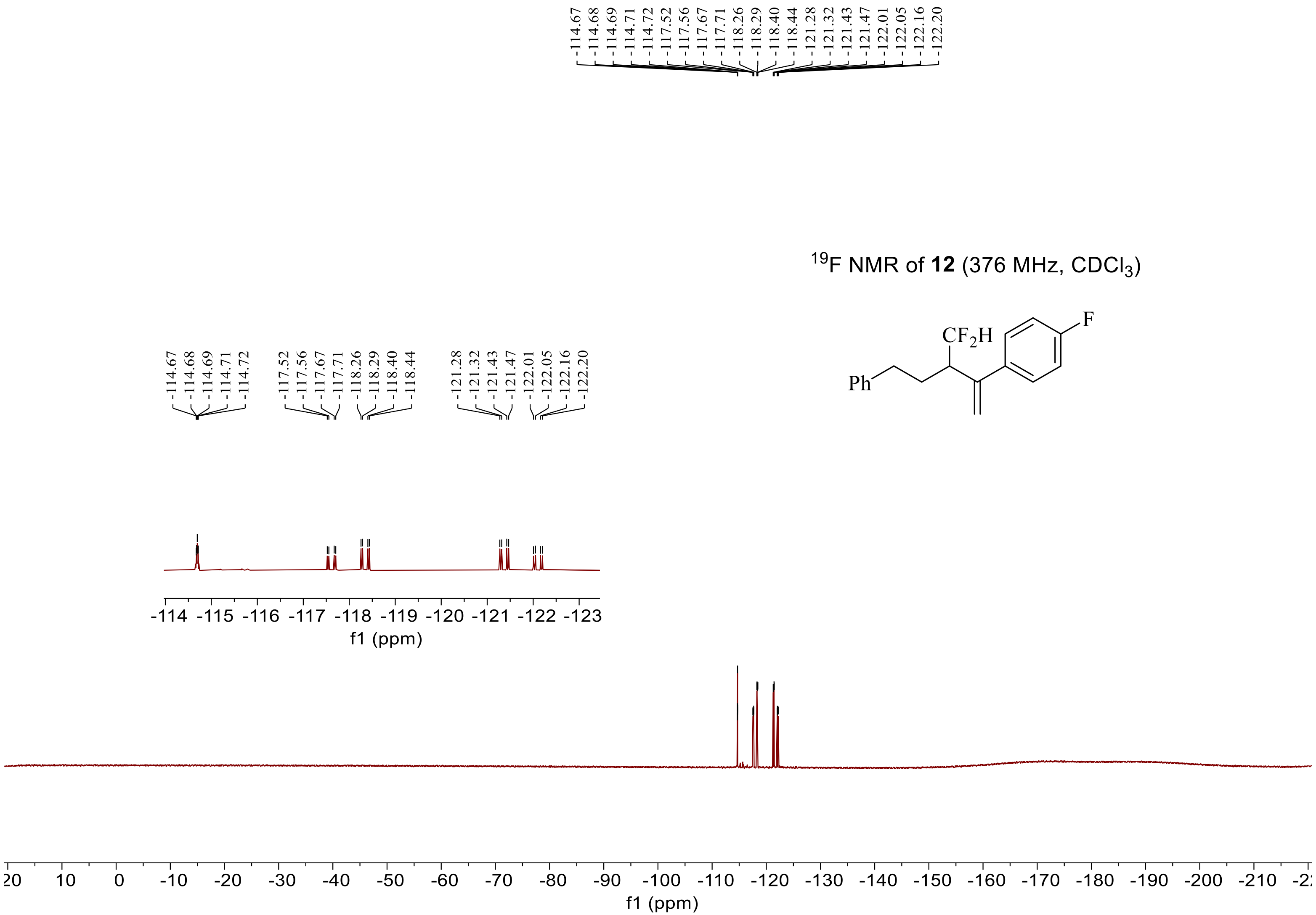
^{19}F NMR of **11** (376 MHz, $CDCl_3$)





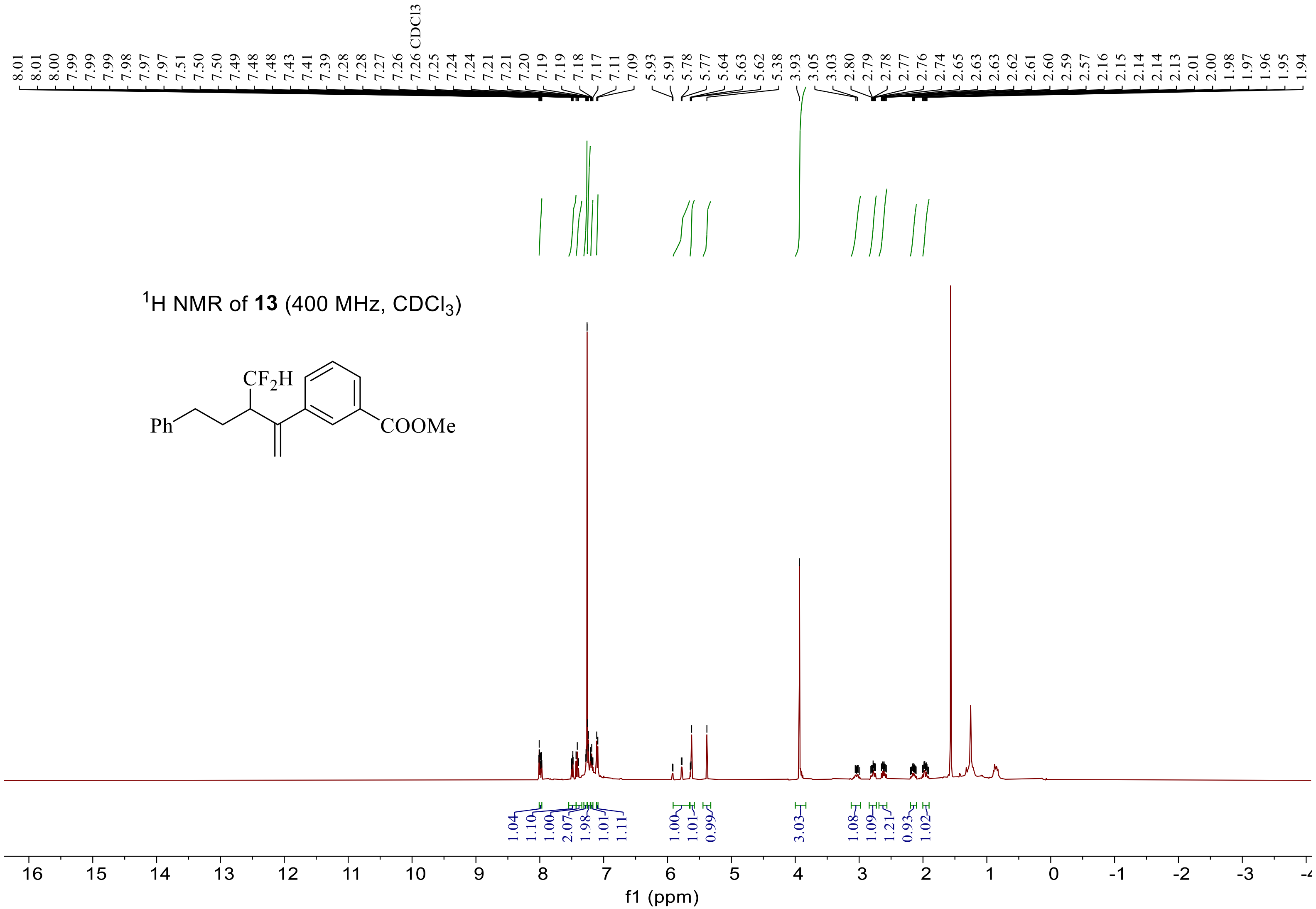

^1H NMR of **12** (400 MHz, $CDCl_3$)
CF_2H
F
Ph
f1 (ppm)


163.82
161.37
144.59
144.55
144.51
141.28
138.28
138.25
128.60
128.54
128.43
128.36
126.26
120.39
117.96
116.48
115.57
115.53
115.35
77.16 CDCl3
47.89
47.70
47.50
32.89
30.20
30.16
30.12
^{13}C NMR of **12** (101 MHz, $CDCl_3$)
CF_2H
F
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

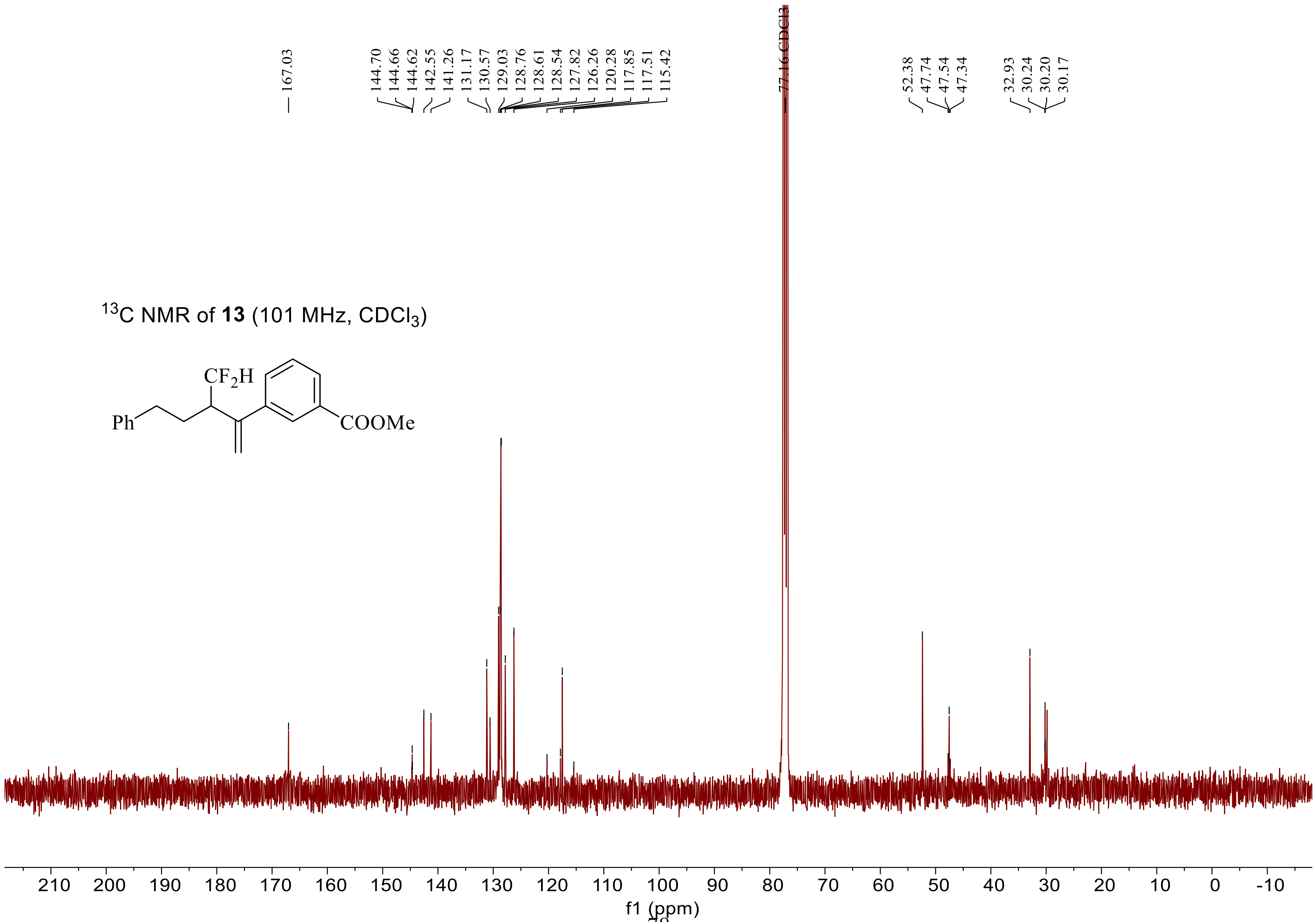


^{19}F NMR of **12** (376 MHz, $CDCl_3$)

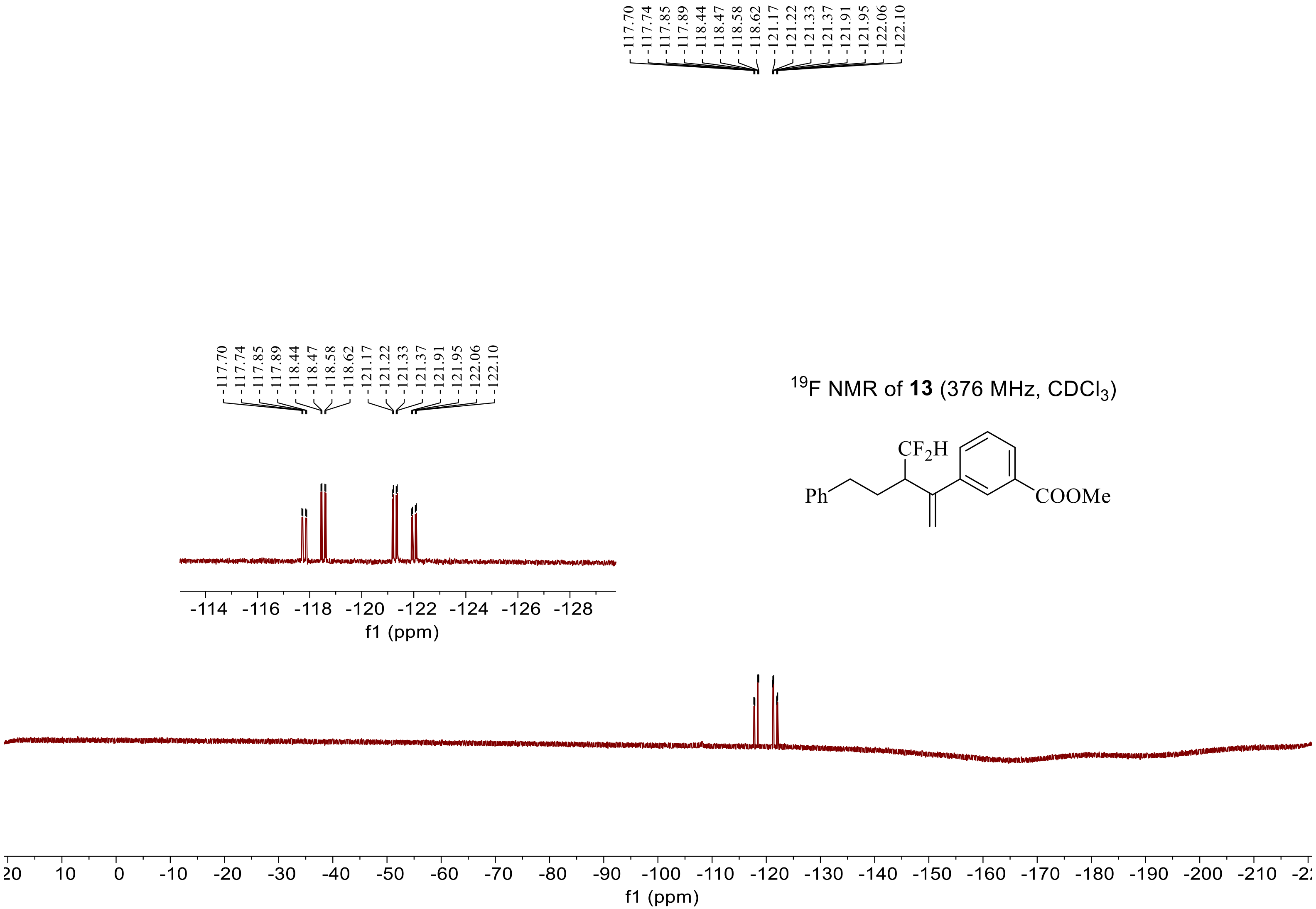
[1]H NMR of **13** (400 MHz, $CDCl_3$)



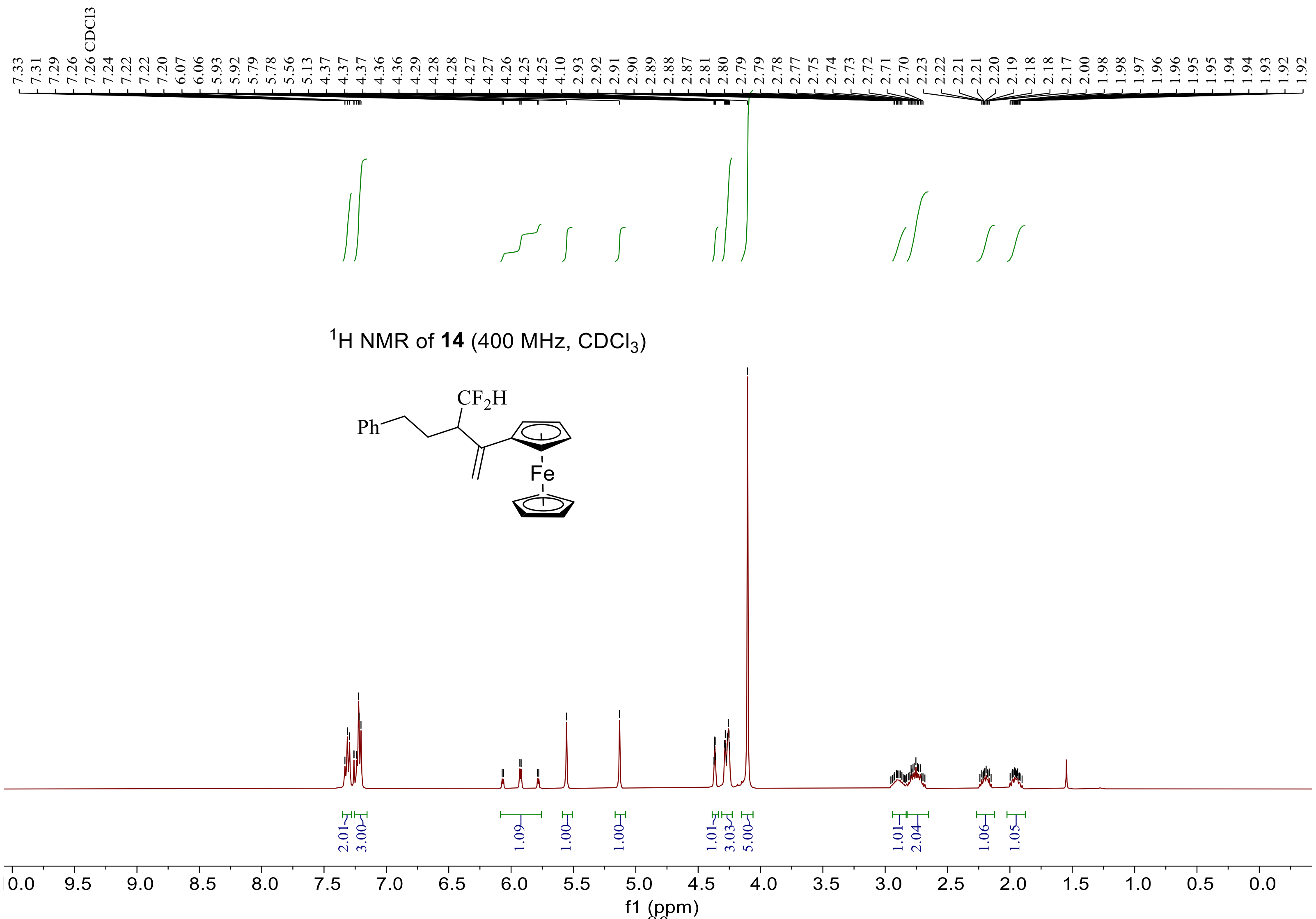
^13^C NMR of **13** (101 MHz, $CDCl_3$)



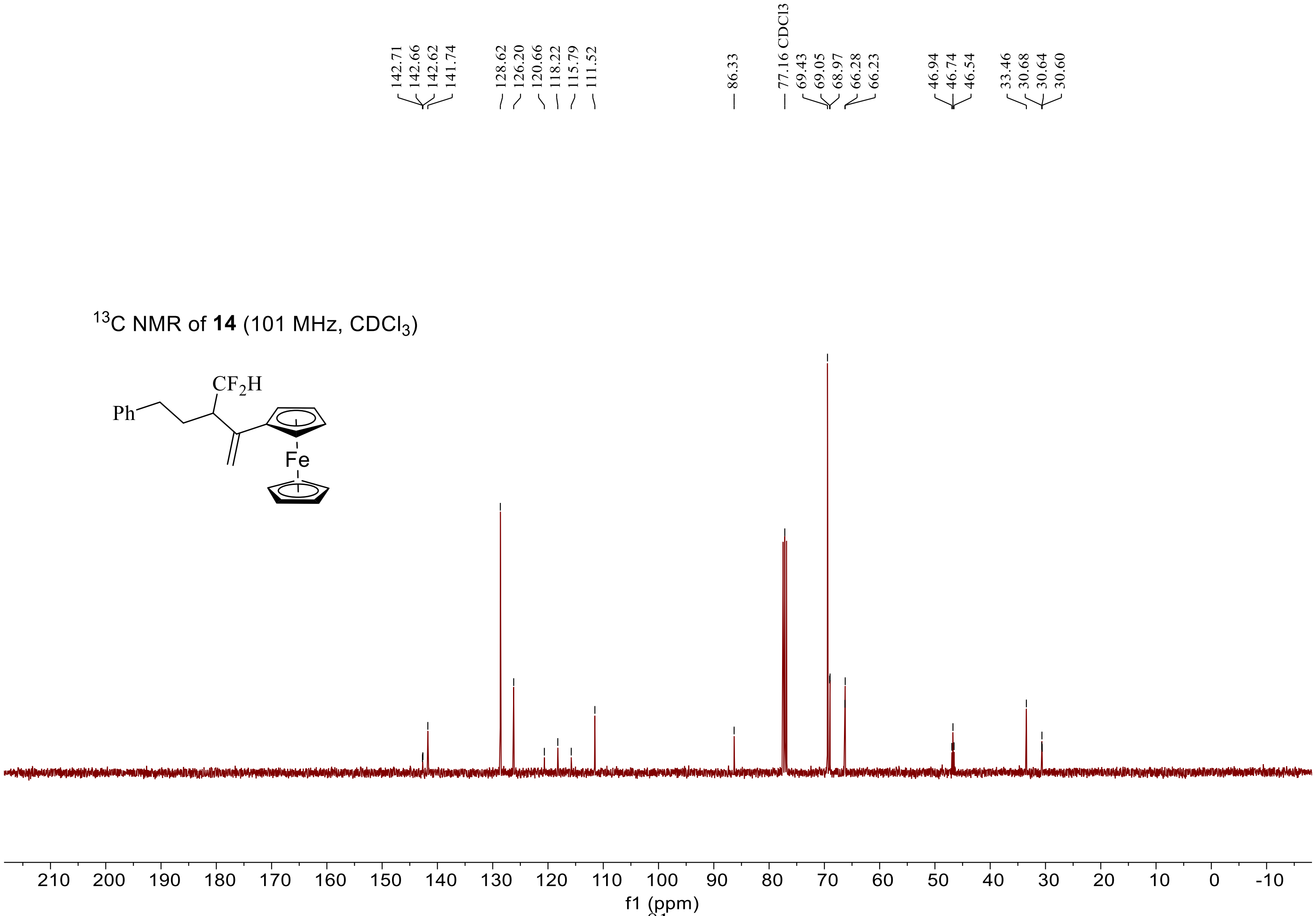
^{19}F NMR of **13** (376 MHz, $CDCl_3$)



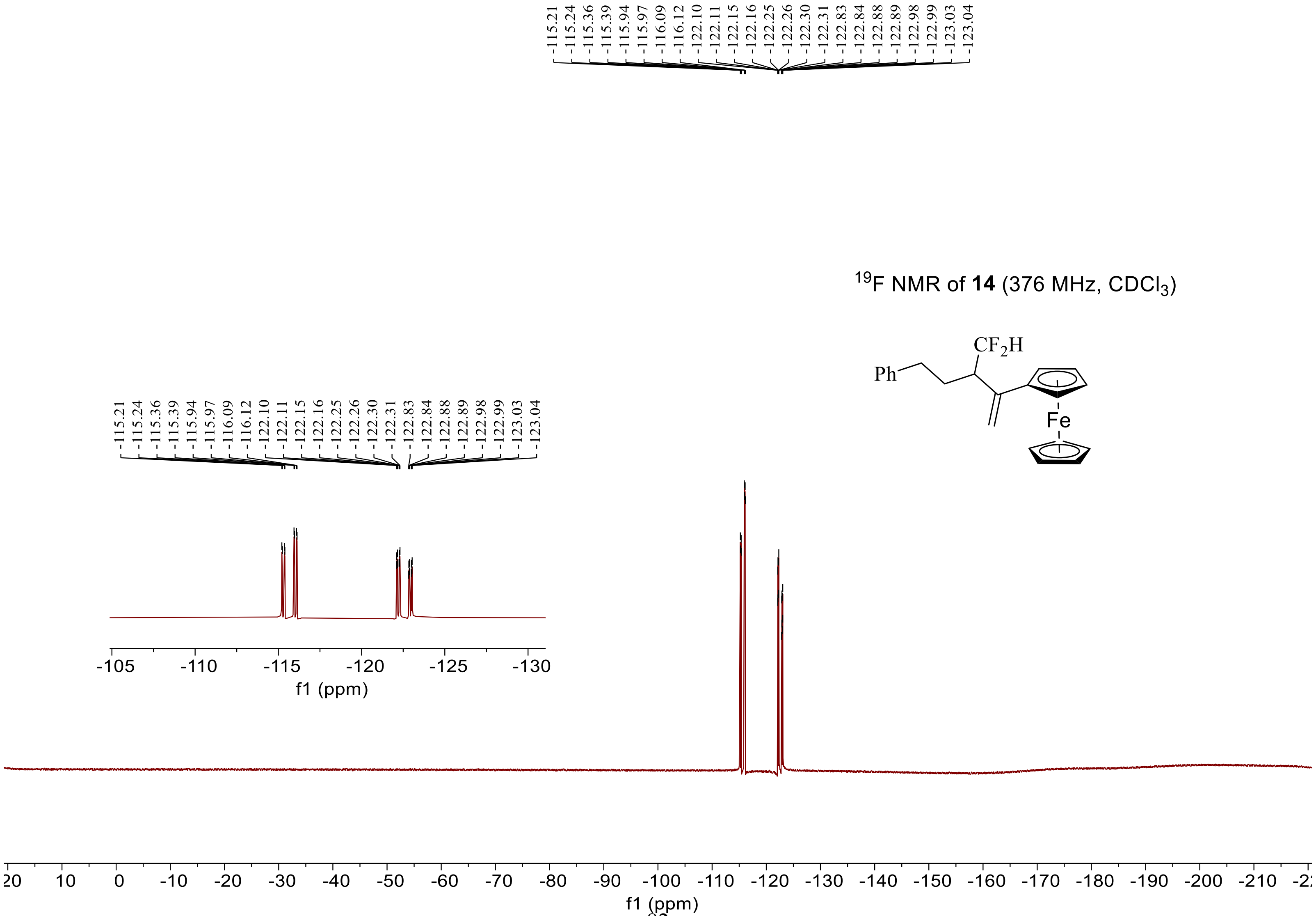
[1]H NMR of **14** (400 MHz, $CDCl_3$)

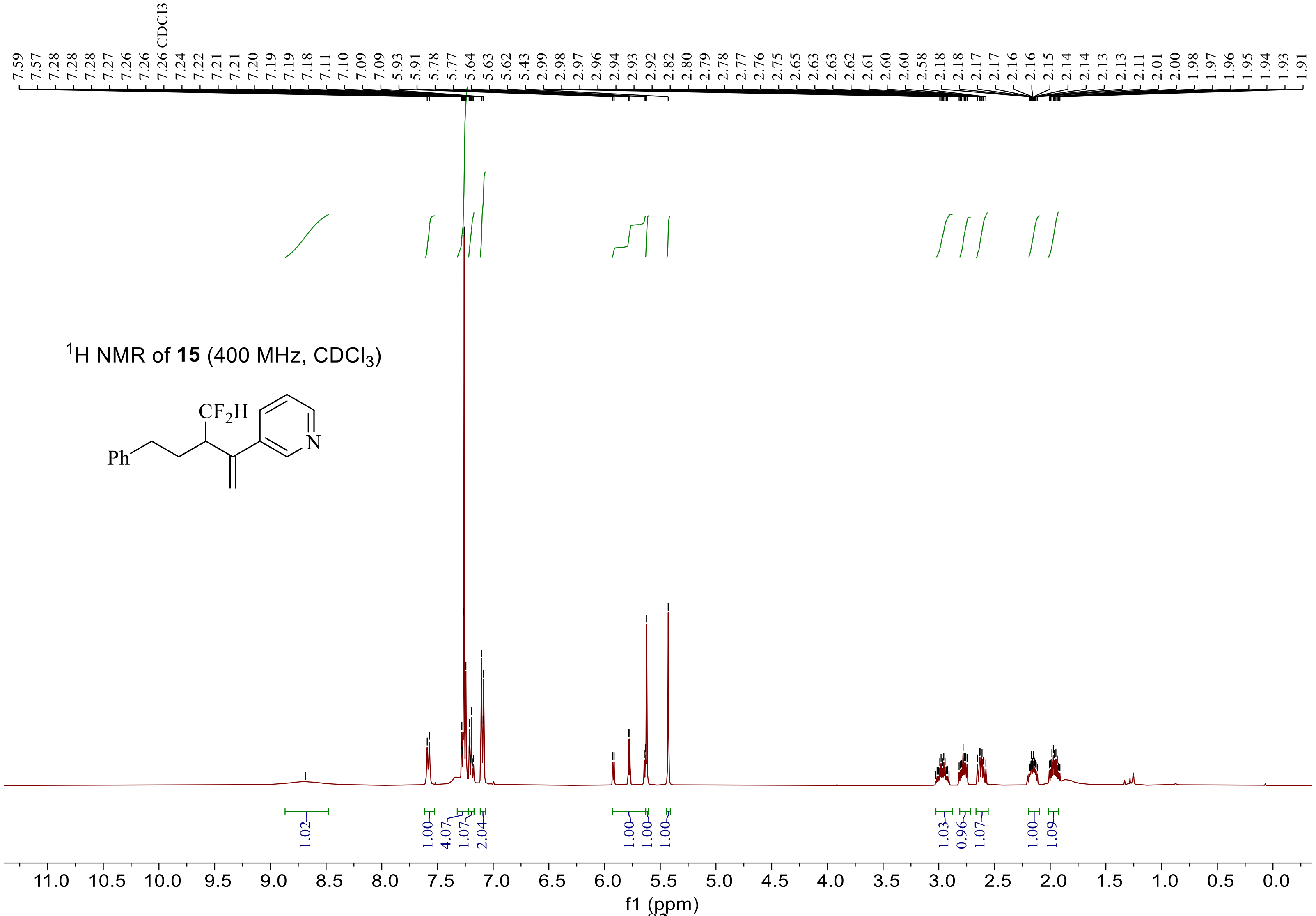


^{13}C NMR of **14** (101 MHz, $CDCl_3$)

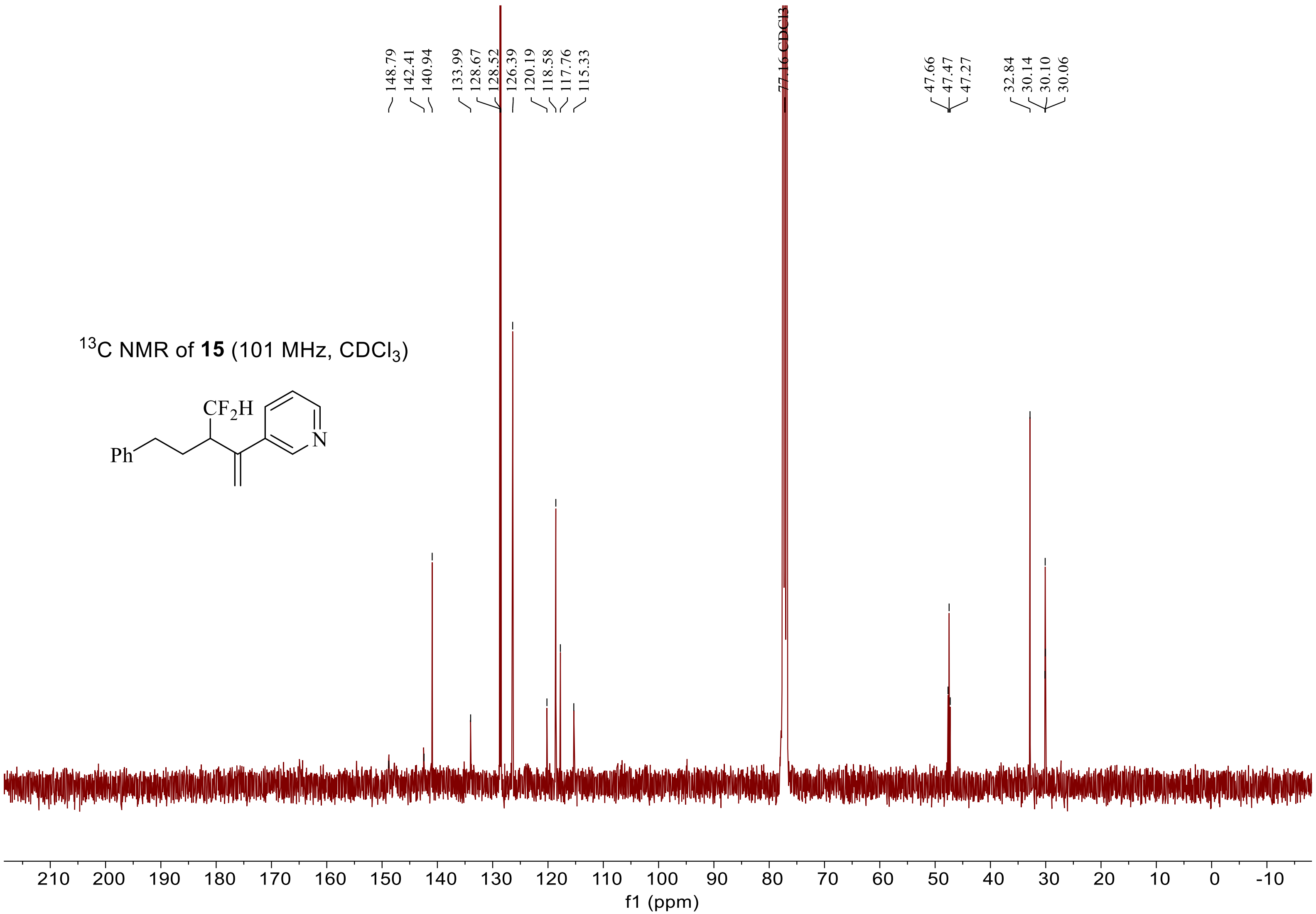


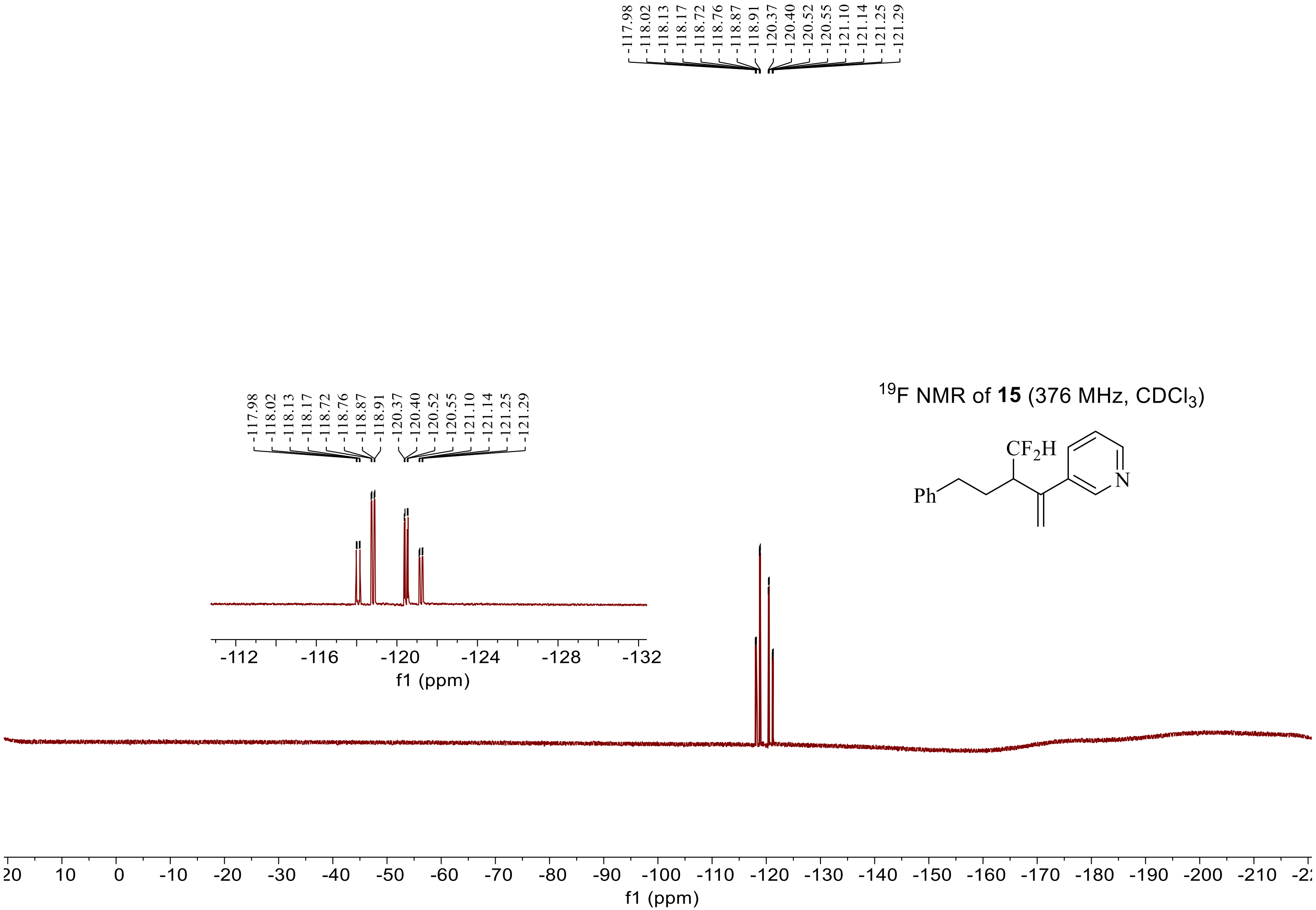
^{19}F NMR of **14** (376 MHz, $CDCl_3$)



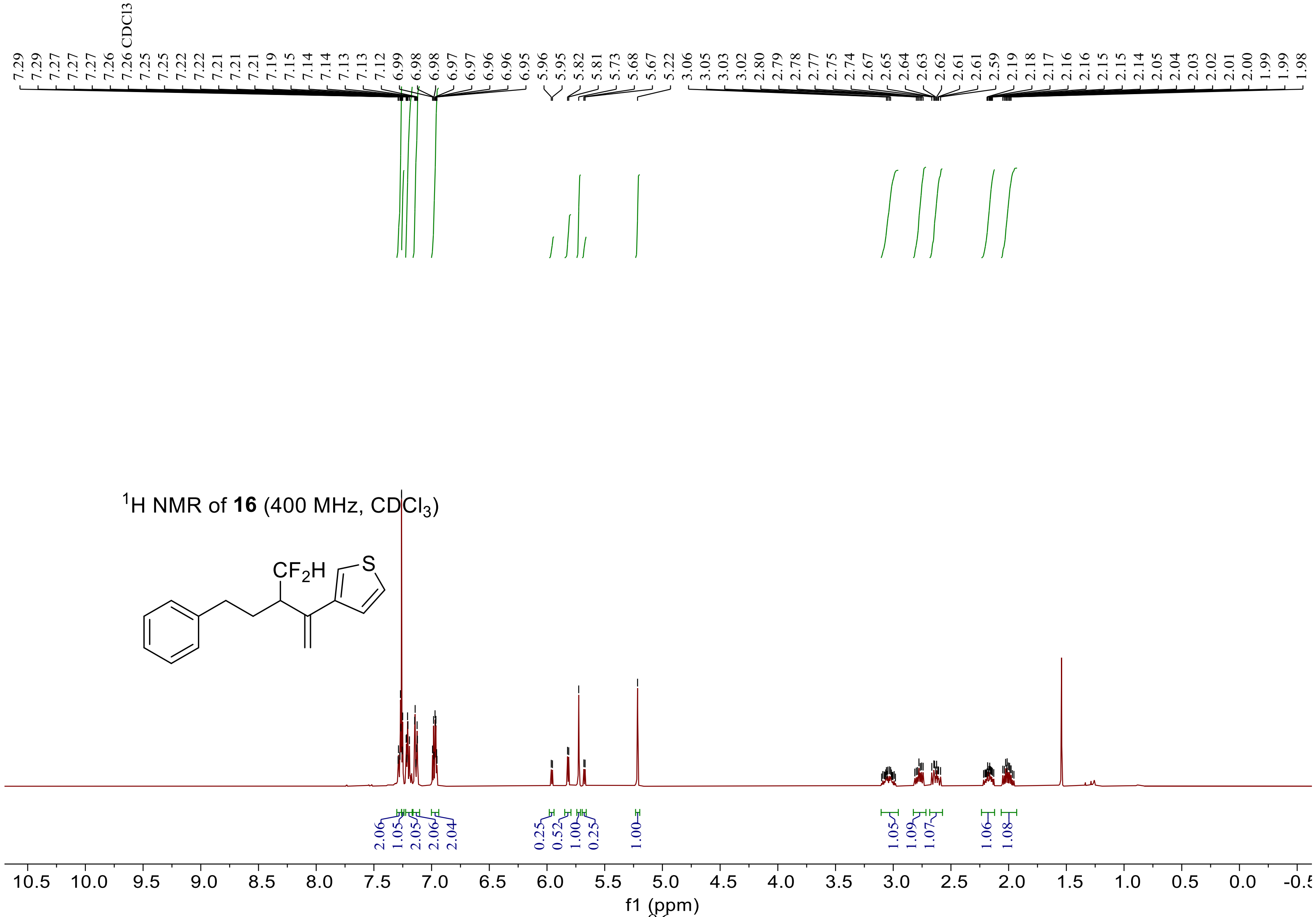


^{1}H NMR of **15** (400 MHz, $CDCl_3$)


13C NMR of 15 (101 MHz, CDCl3)
CF2H
Ph
N
148.79
142.41
140.94
133.99
128.67
128.52
126.39
120.19
118.58
117.76
115.33
77.16 CDCl3
47.66
47.47
47.27
32.84
30.14
30.10
30.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

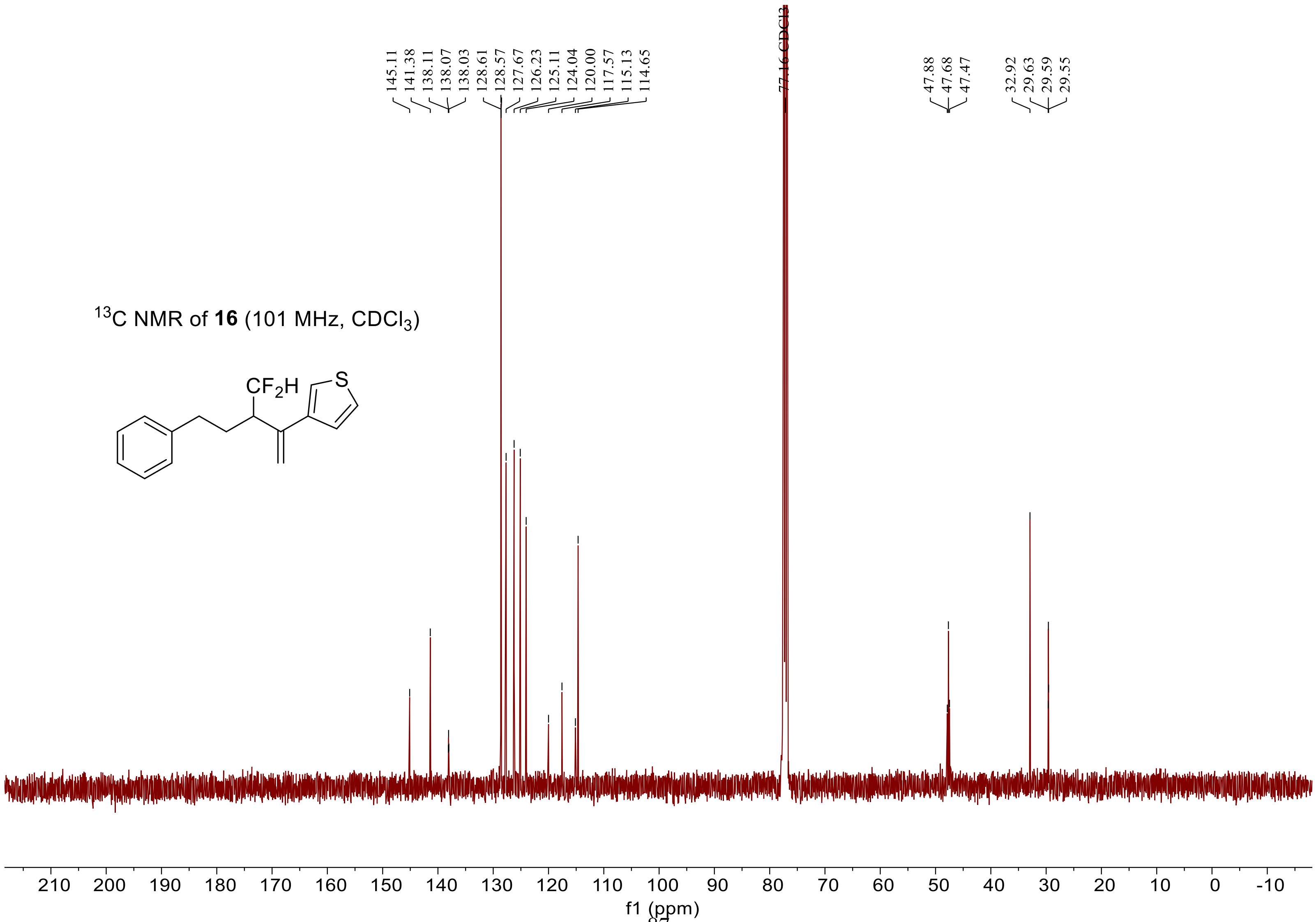


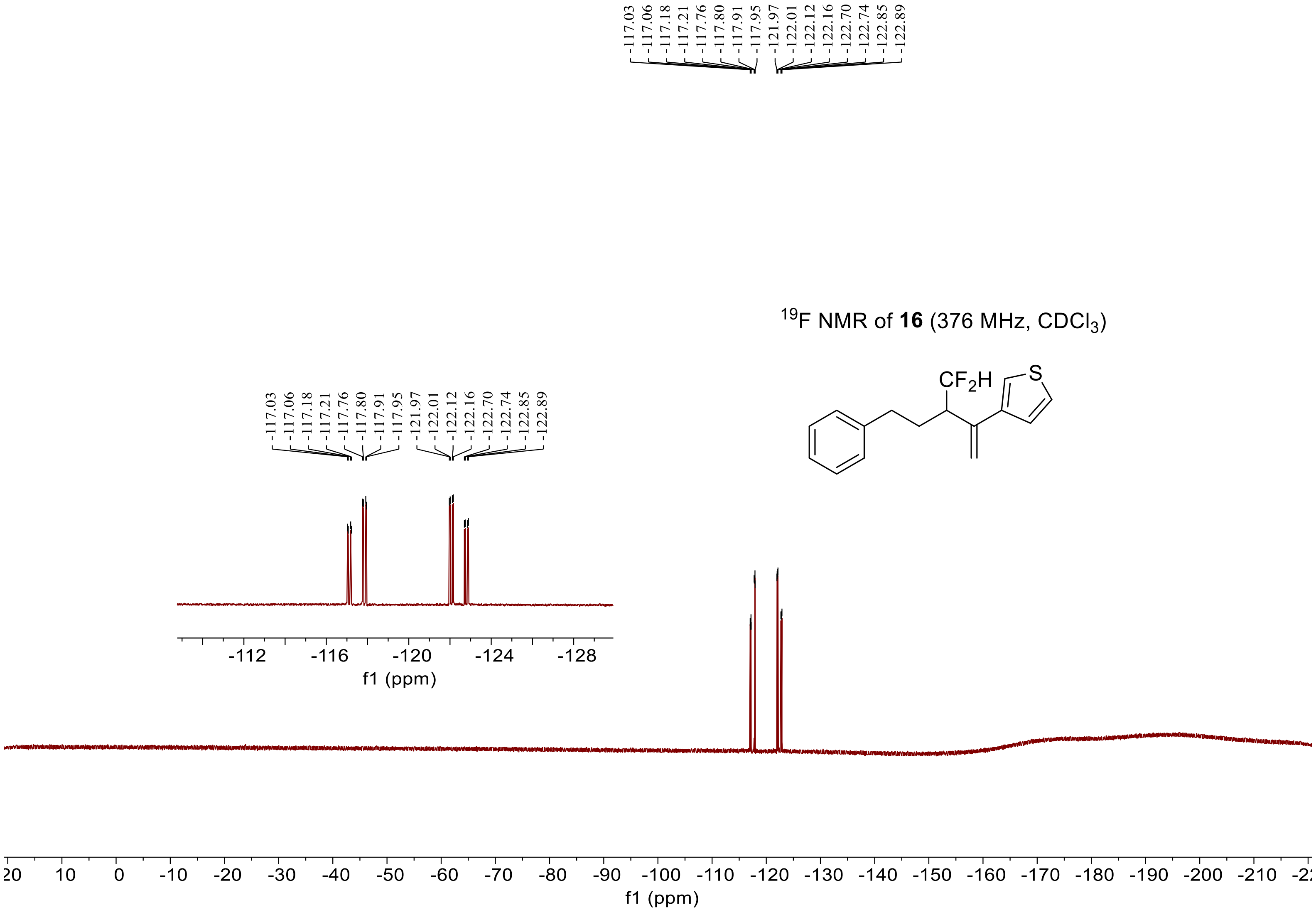
^{19}F NMR of **15** (376 MHz, $CDCl_3$)



^{1}H NMR of **16** (400 MHz, CDCl$_3$)
CF$_2$H
S
f1 (ppm)

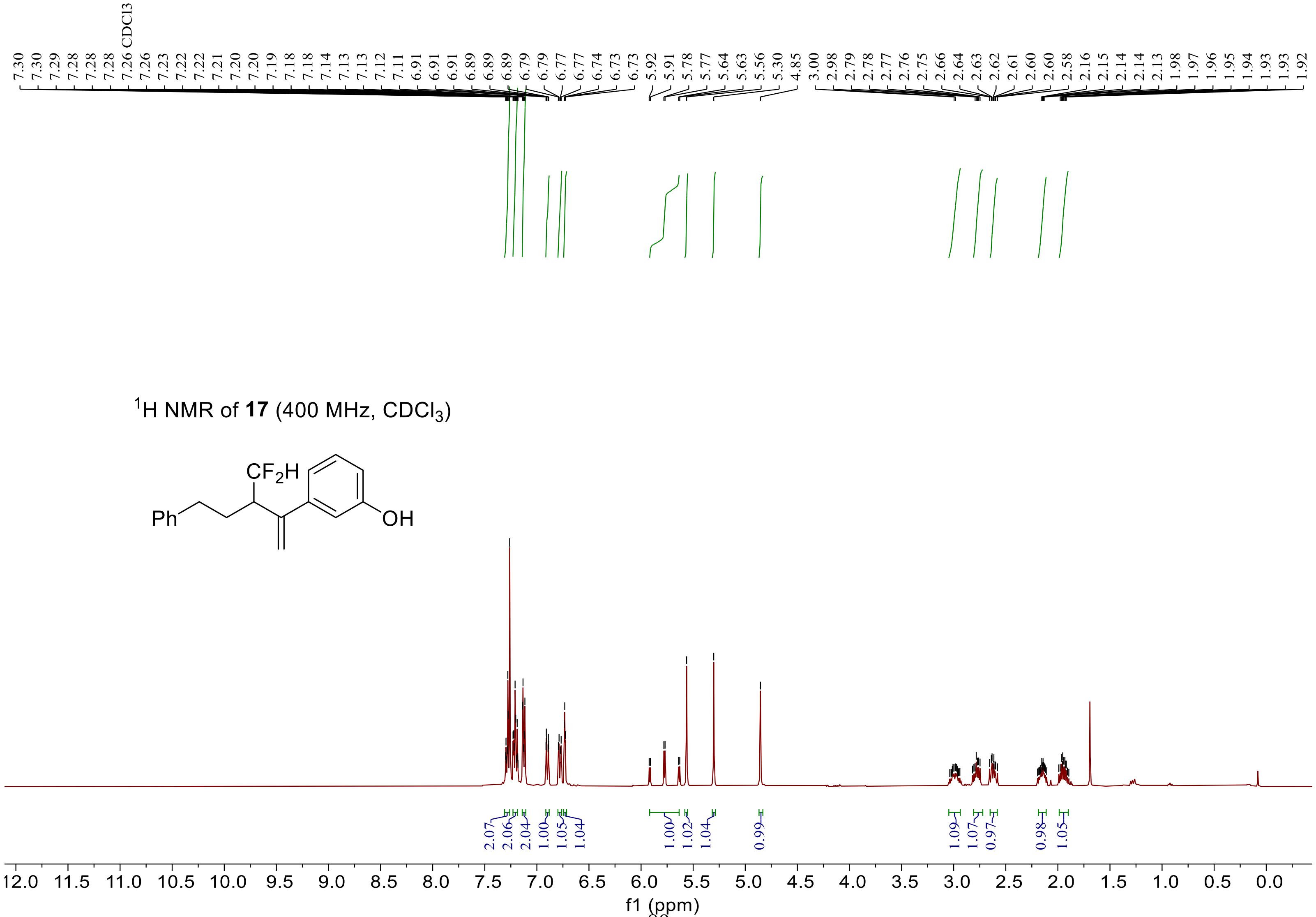
^{13}C NMR of **16** (101 MHz, $CDCl_3$)

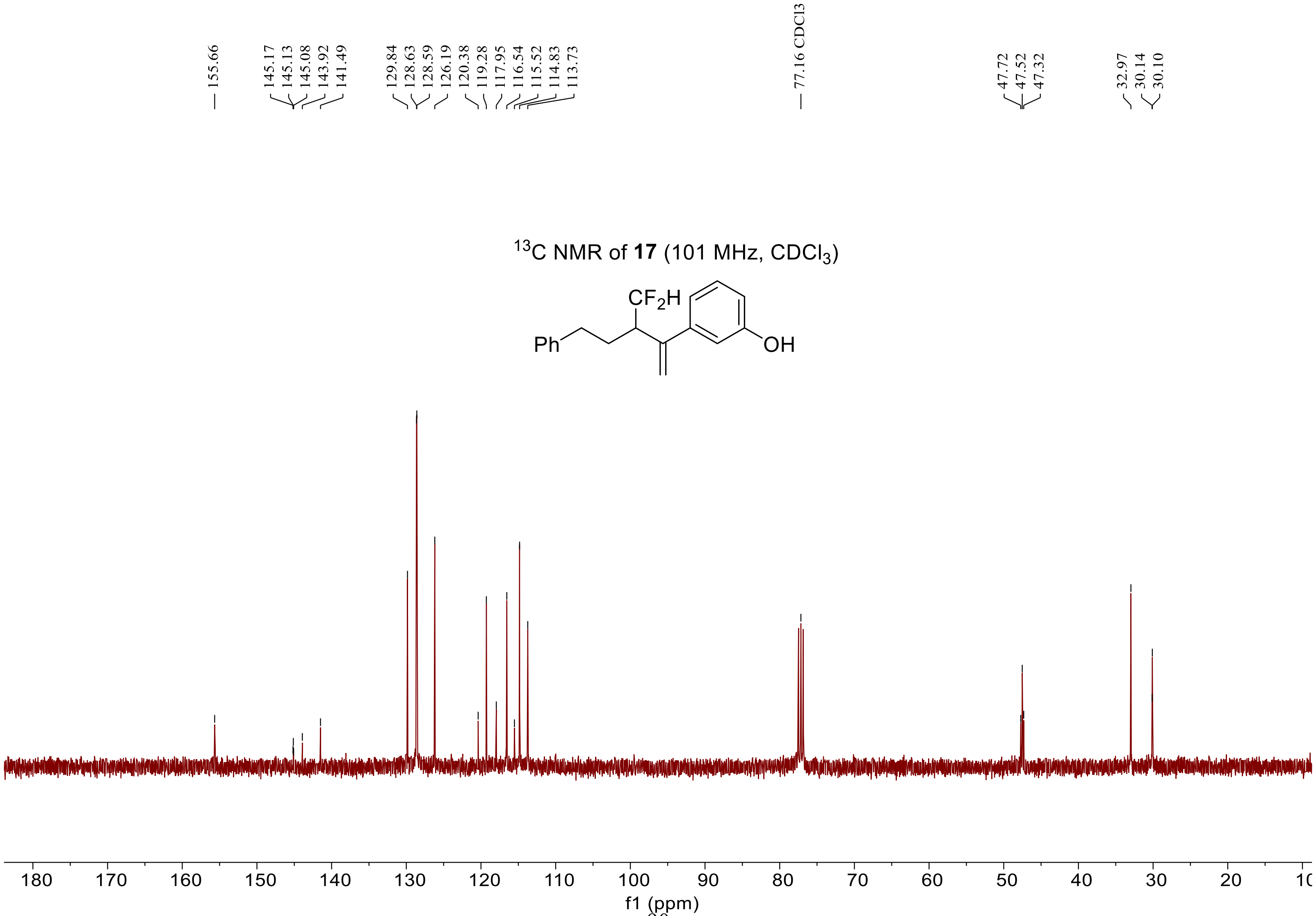




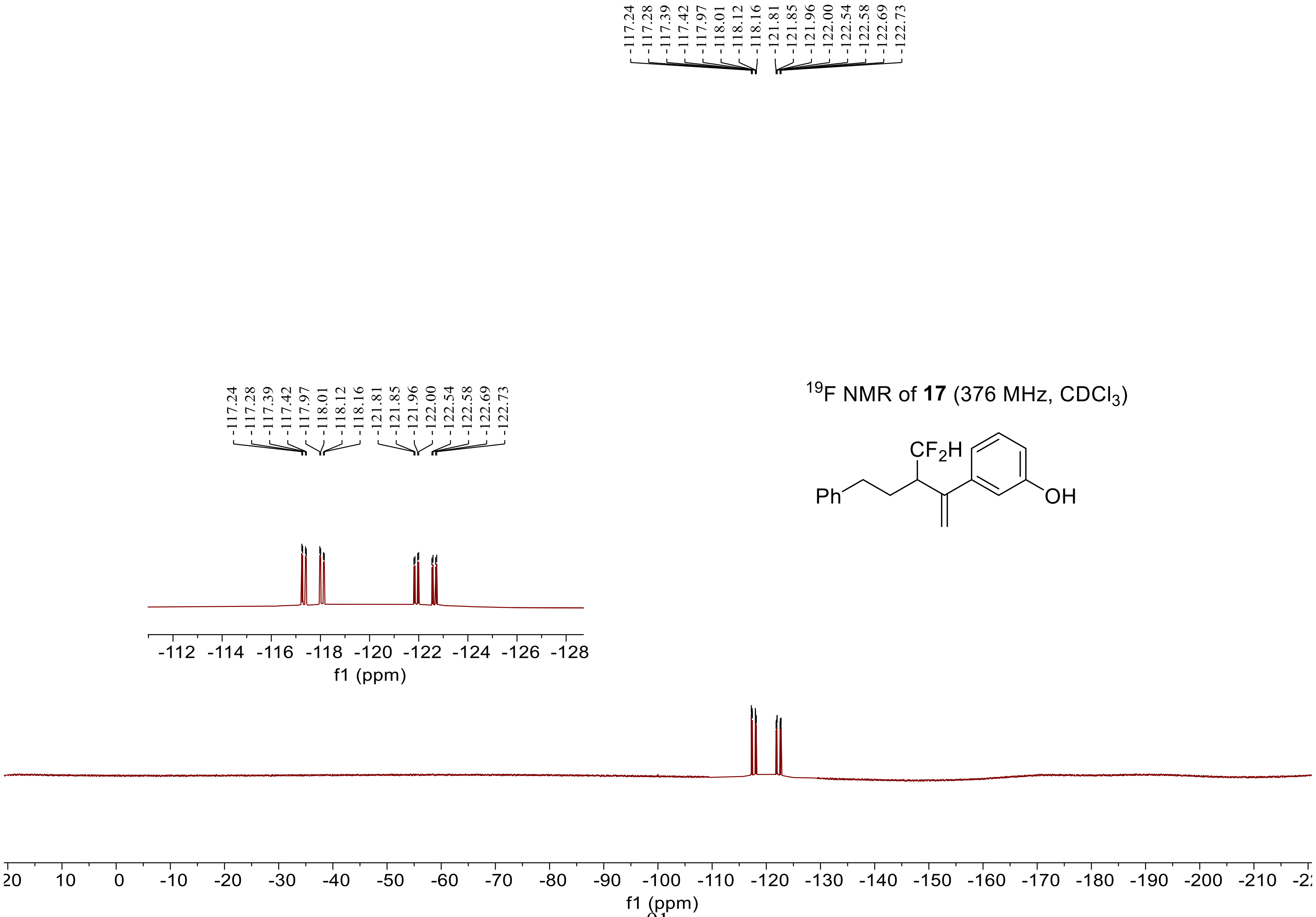
^{19}F NMR of **16** (376 MHz, $CDCl_3$)

^{1}H NMR of **17** (400 MHz, $CDCl_3$)



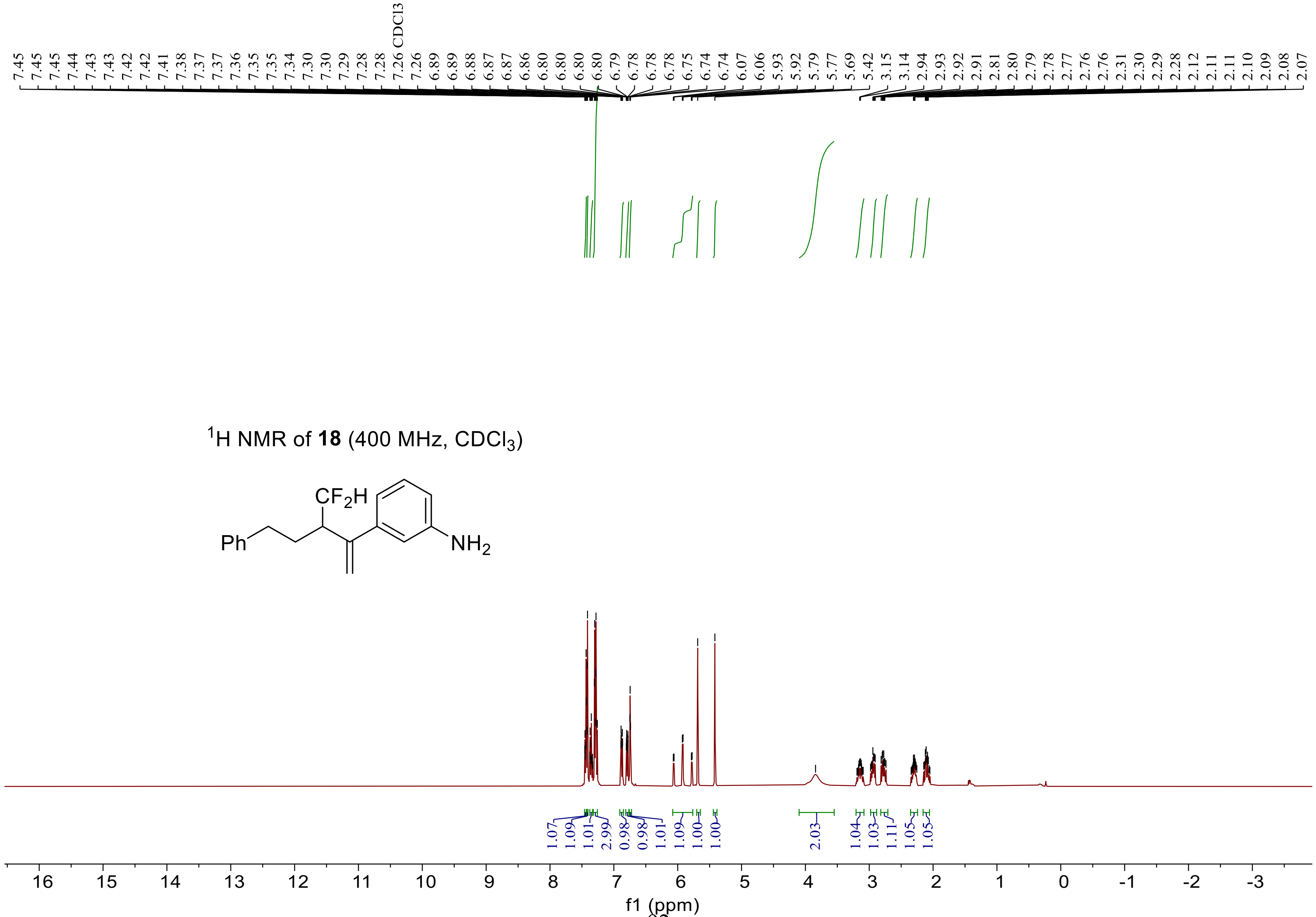


^{13}C NMR of **17** (101 MHz, $CDCl_3$)

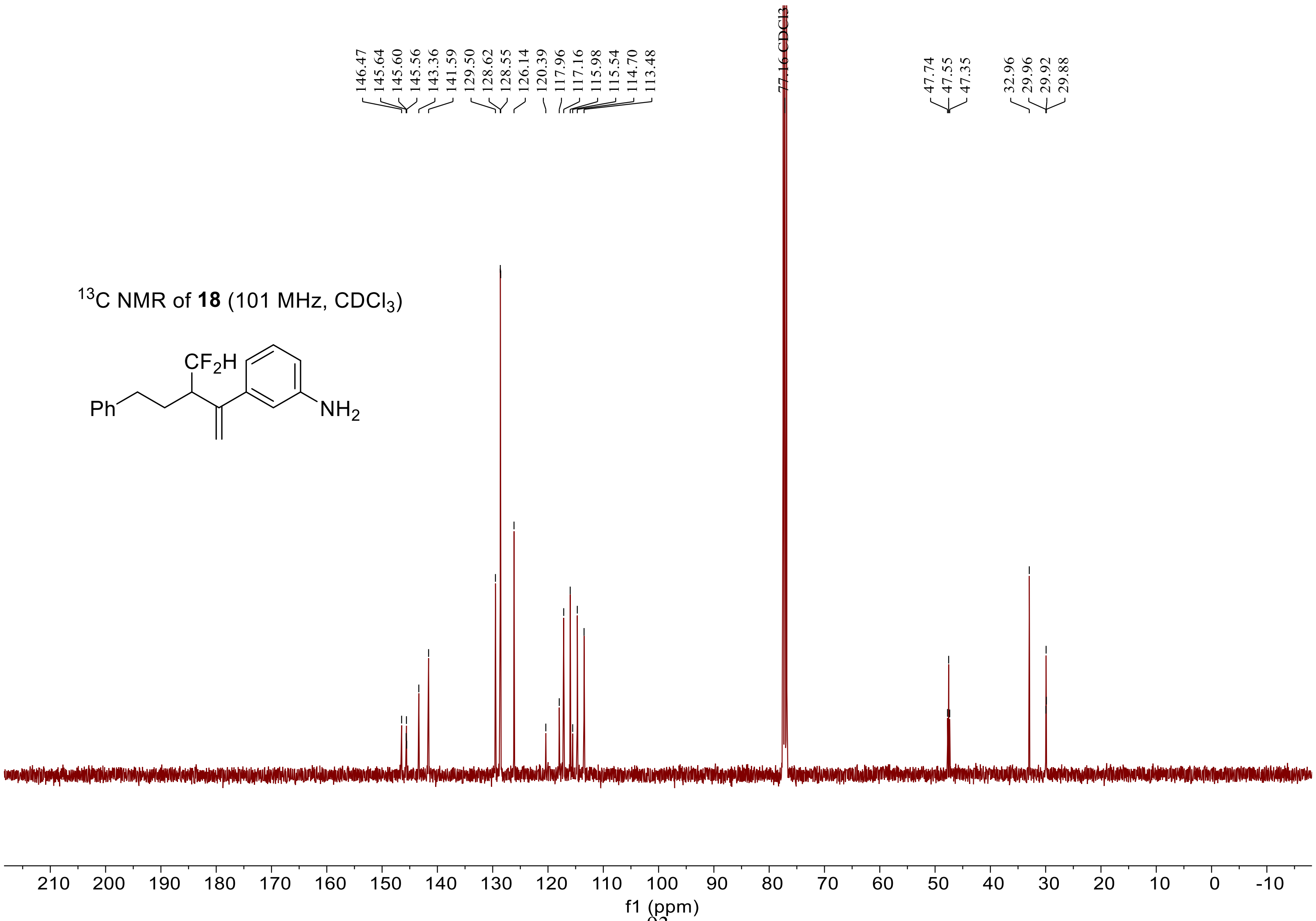


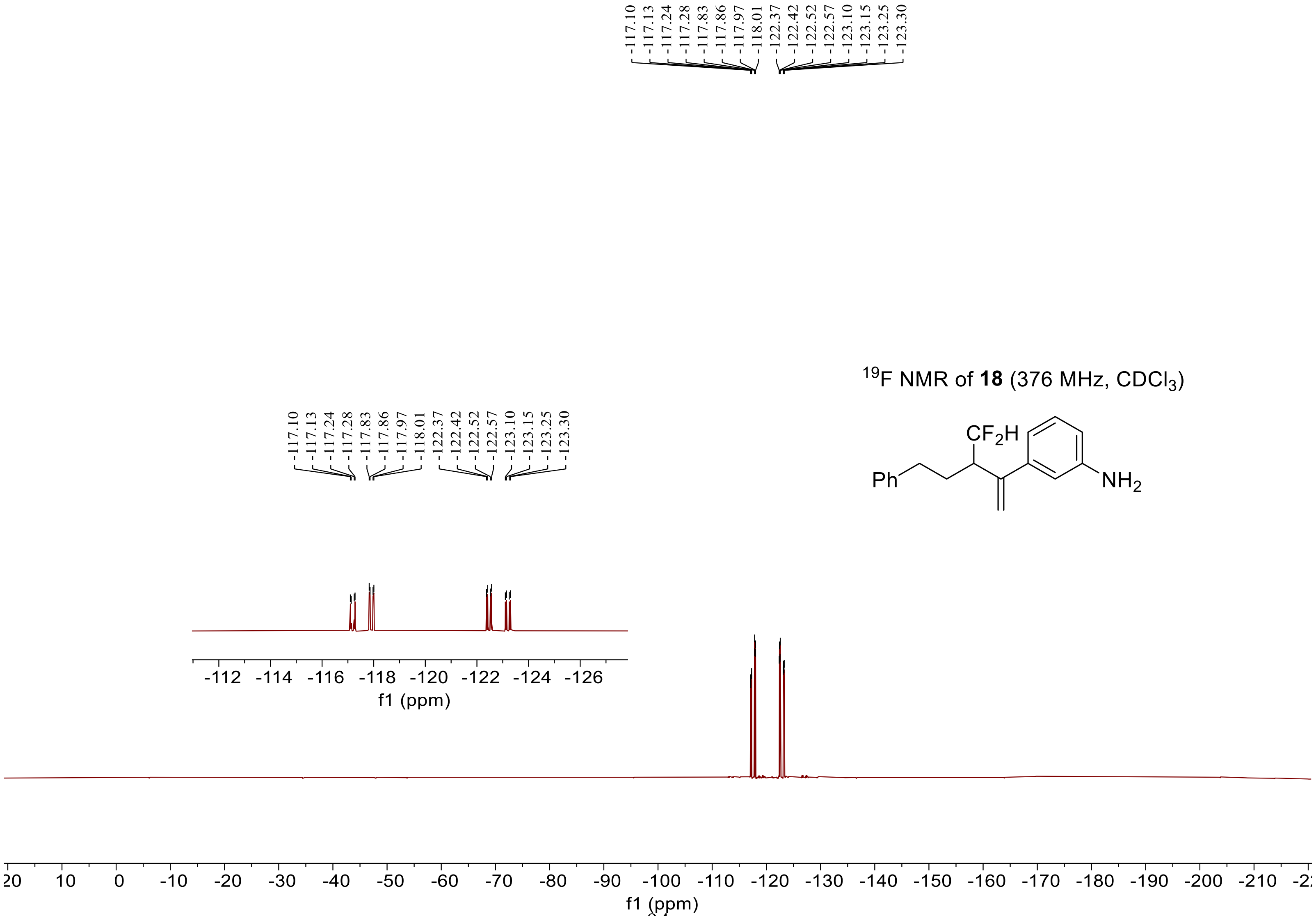
^{19}F NMR of **17** (376 MHz, $CDCl_3$)

^{1}H NMR of **18** (400 MHz, $CDCl_3$)

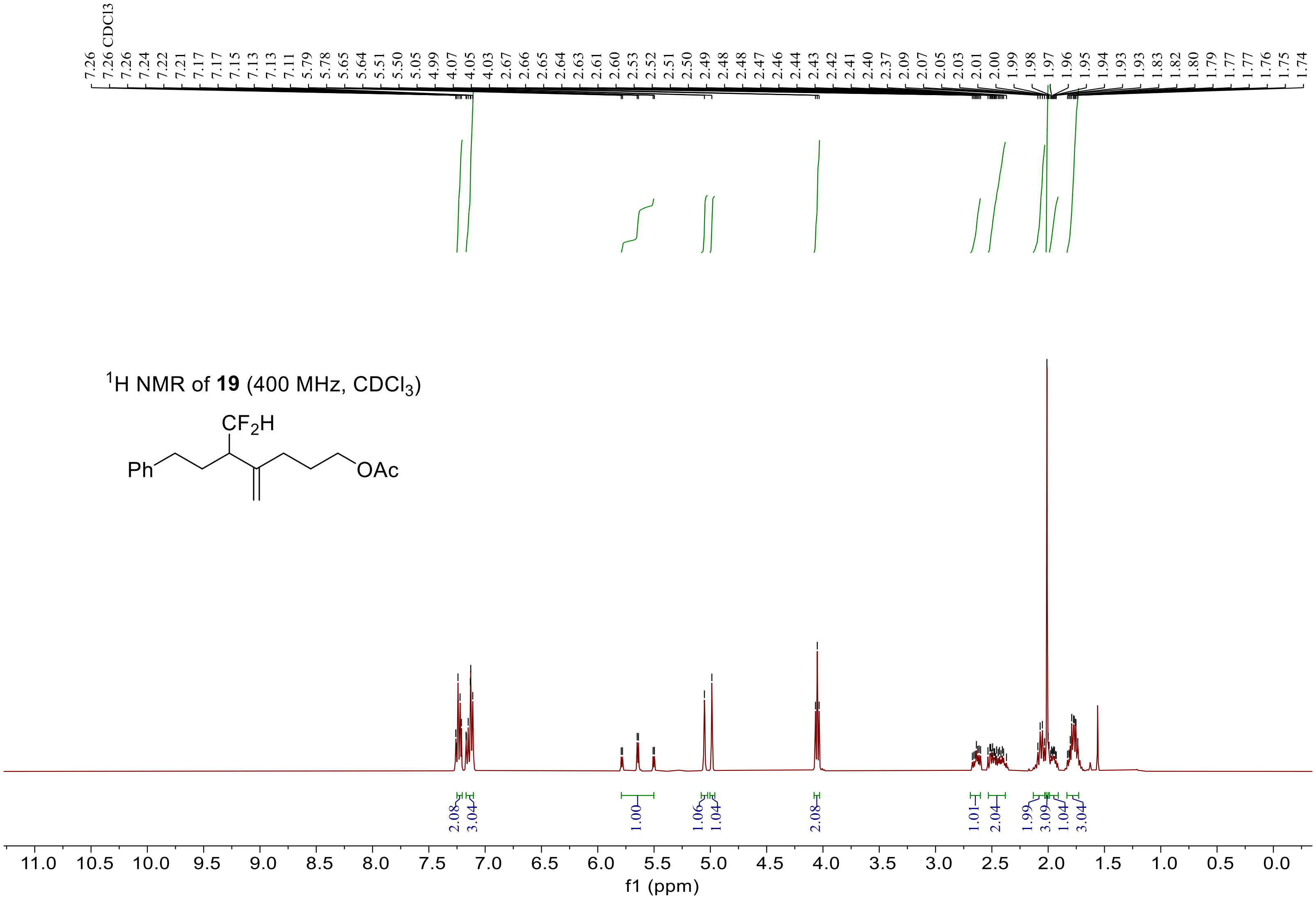


^{13}C NMR of **18** (101 MHz, $CDCl_3$)

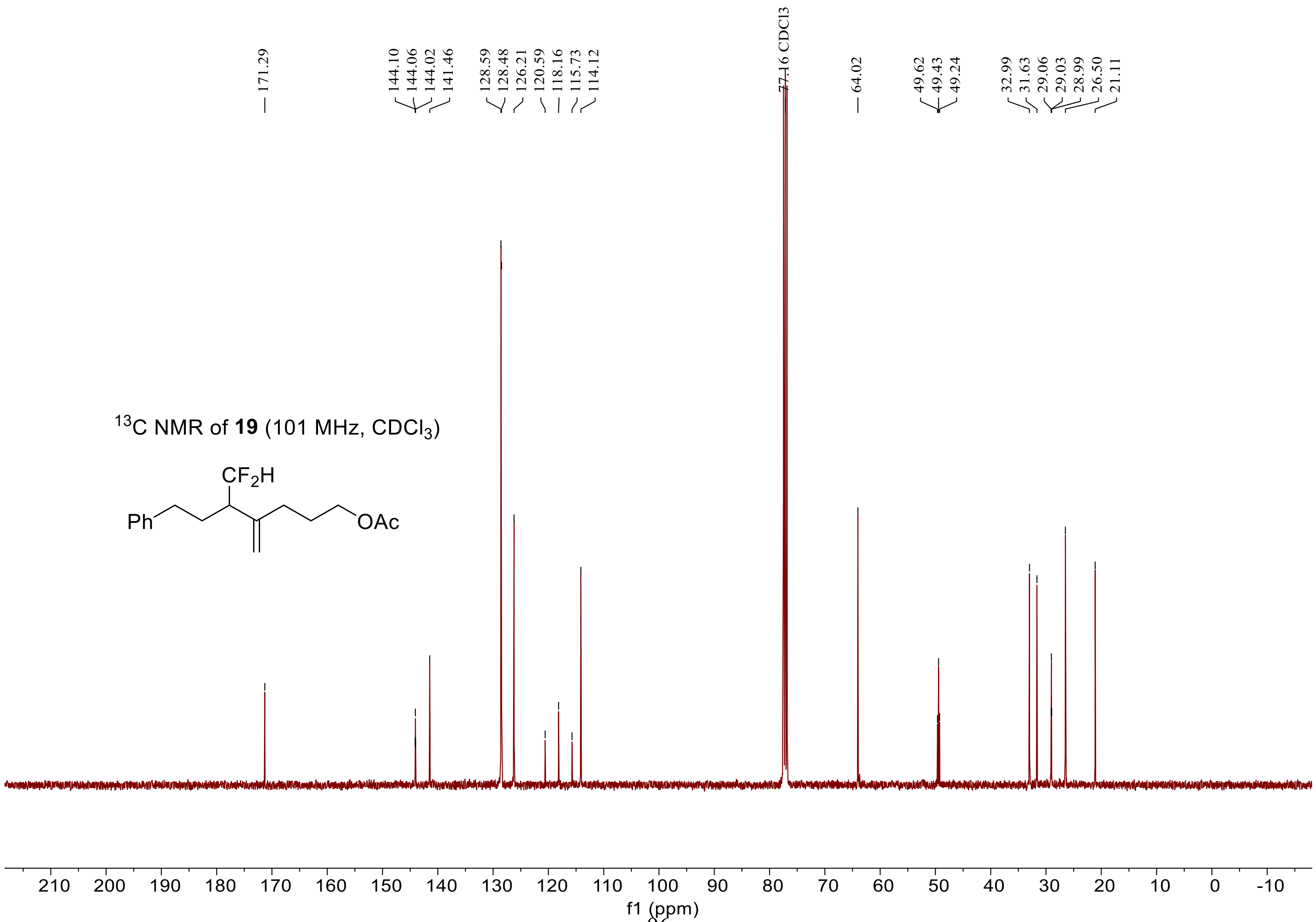


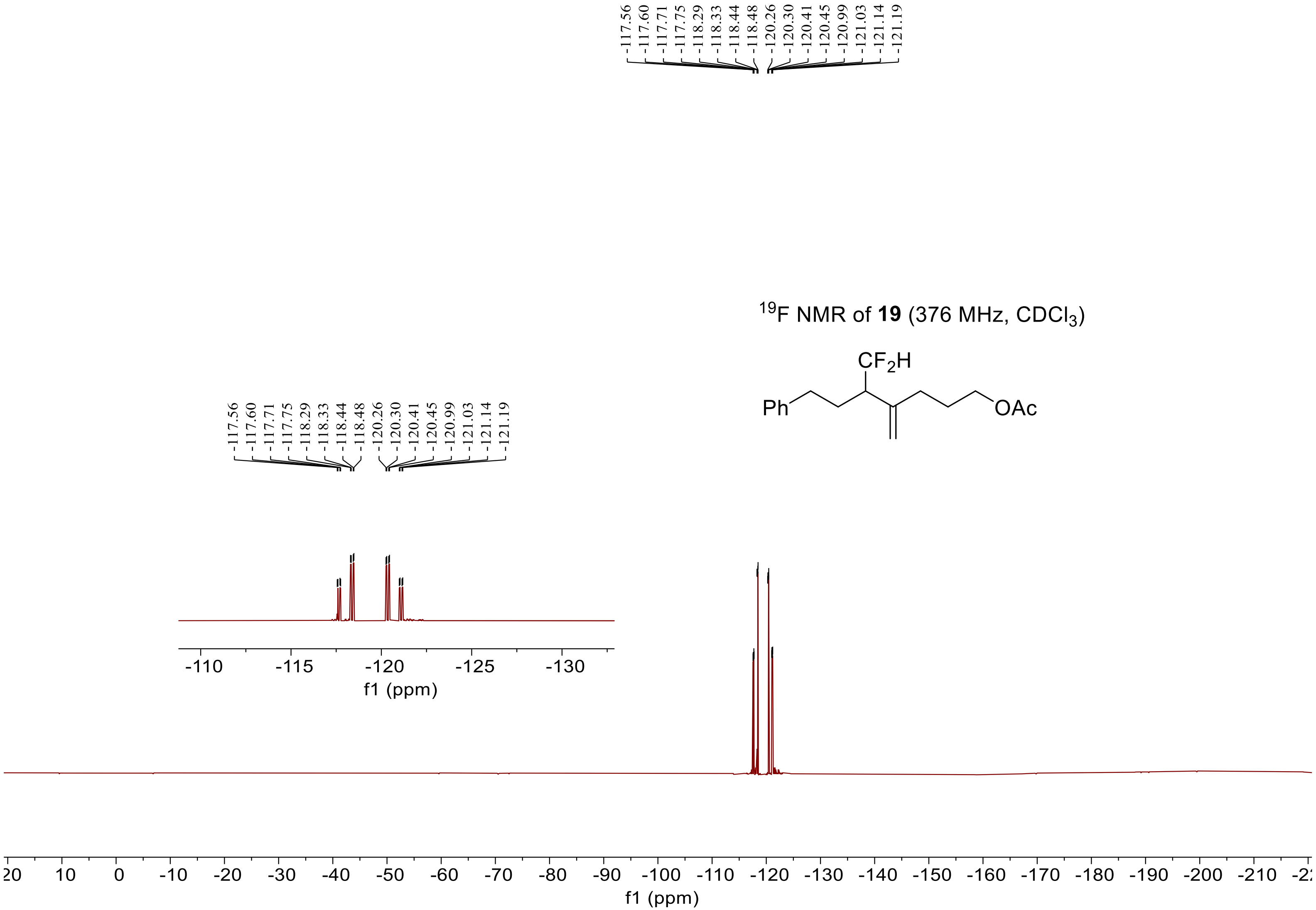


^{19}F NMR of **18** (376 MHz, $CDCl_3$)

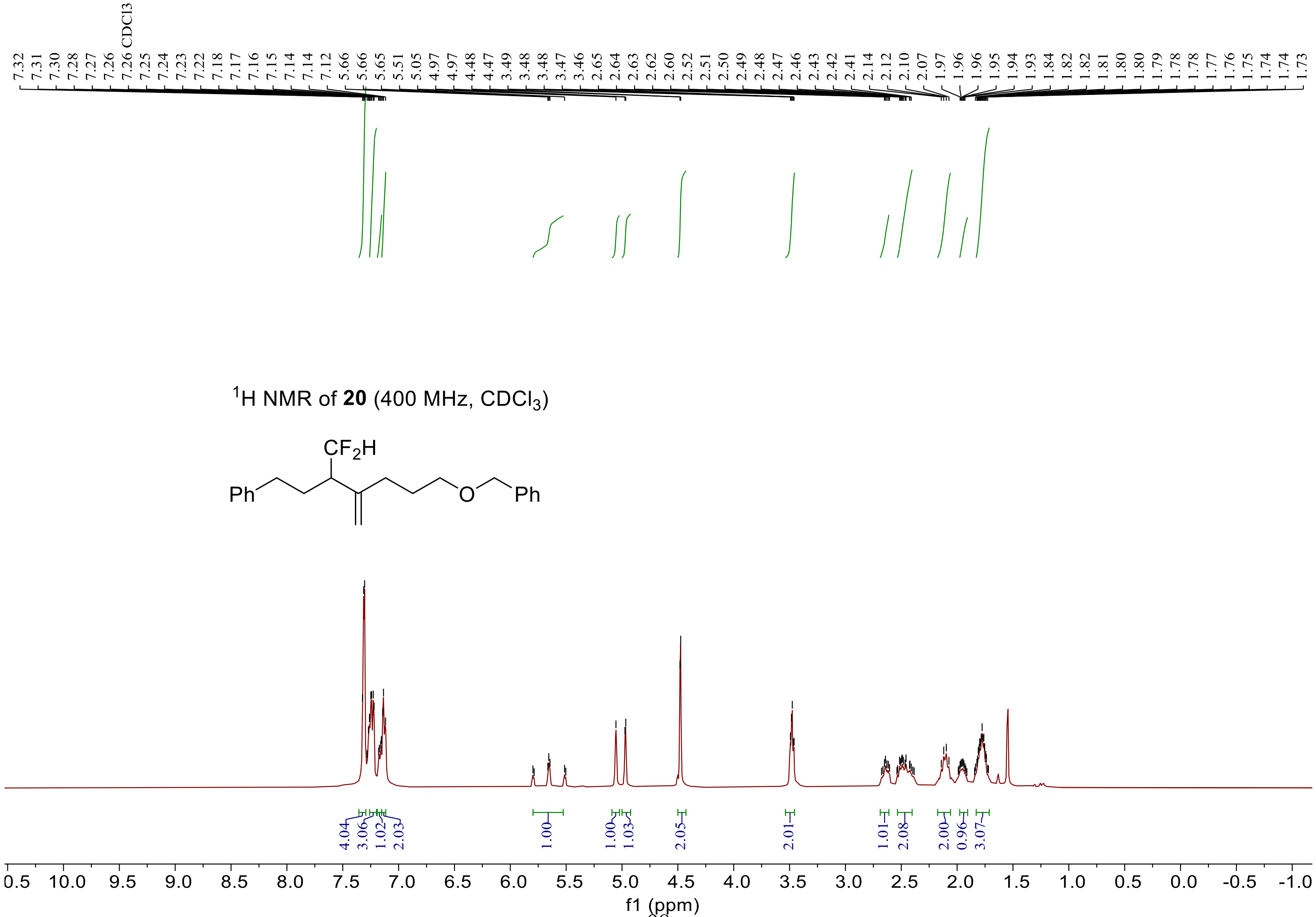


^{1}H NMR of **19** (400 MHz, $CDCl_3$)
CF_2H
Ph
OAc
f1 (ppm)

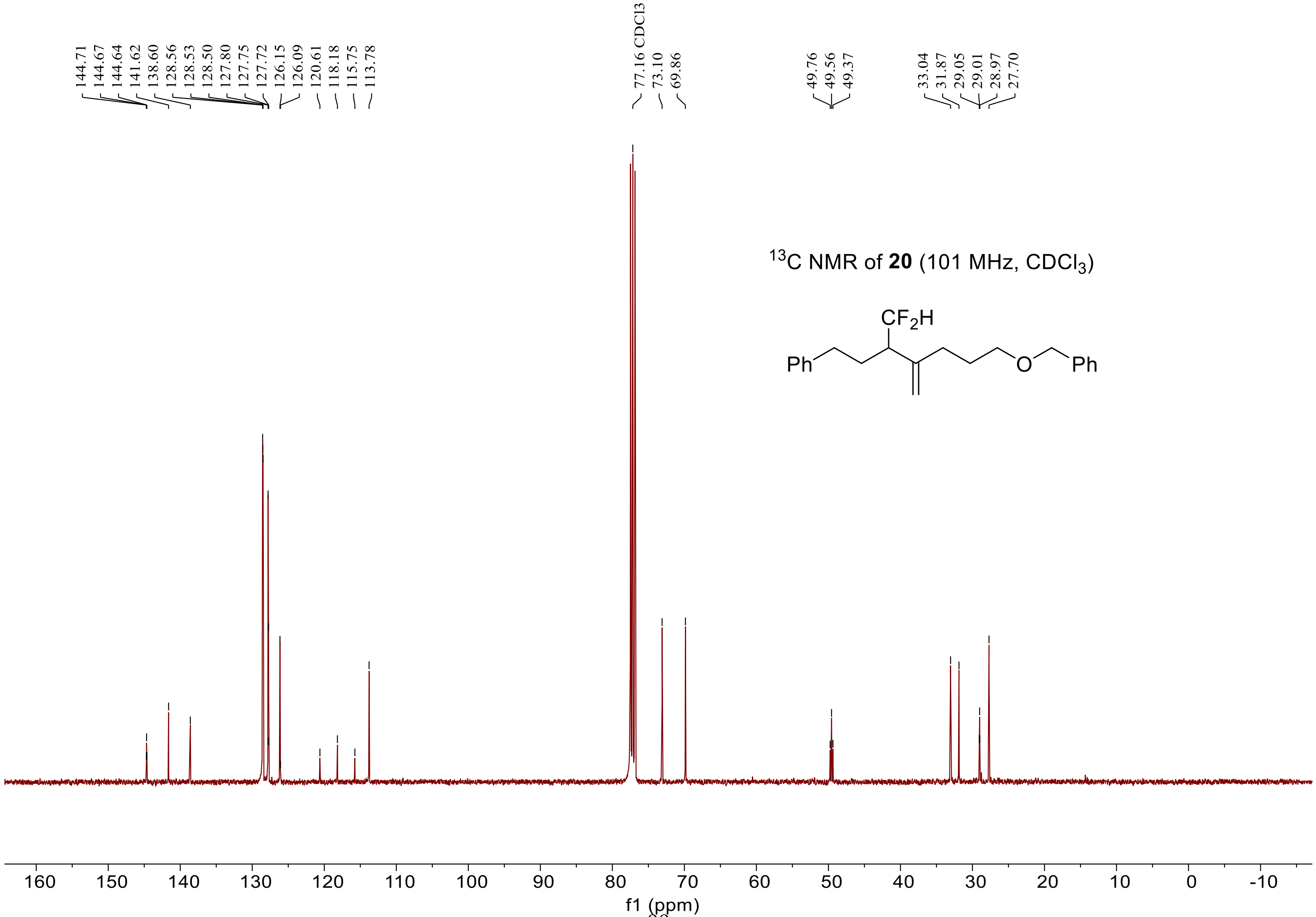

171.29
144.10
144.06
144.02
141.46
128.59
128.48
126.21
120.59
118.16
115.73
114.12
77.16 CDCl3
64.02
49.62
49.43
49.24
32.99
31.63
29.06
29.03
28.99
26.50
21.11
^{13}C NMR of **19** (101 MHz, CDCl$_3$)
CF$_2$H
Ph
OAc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



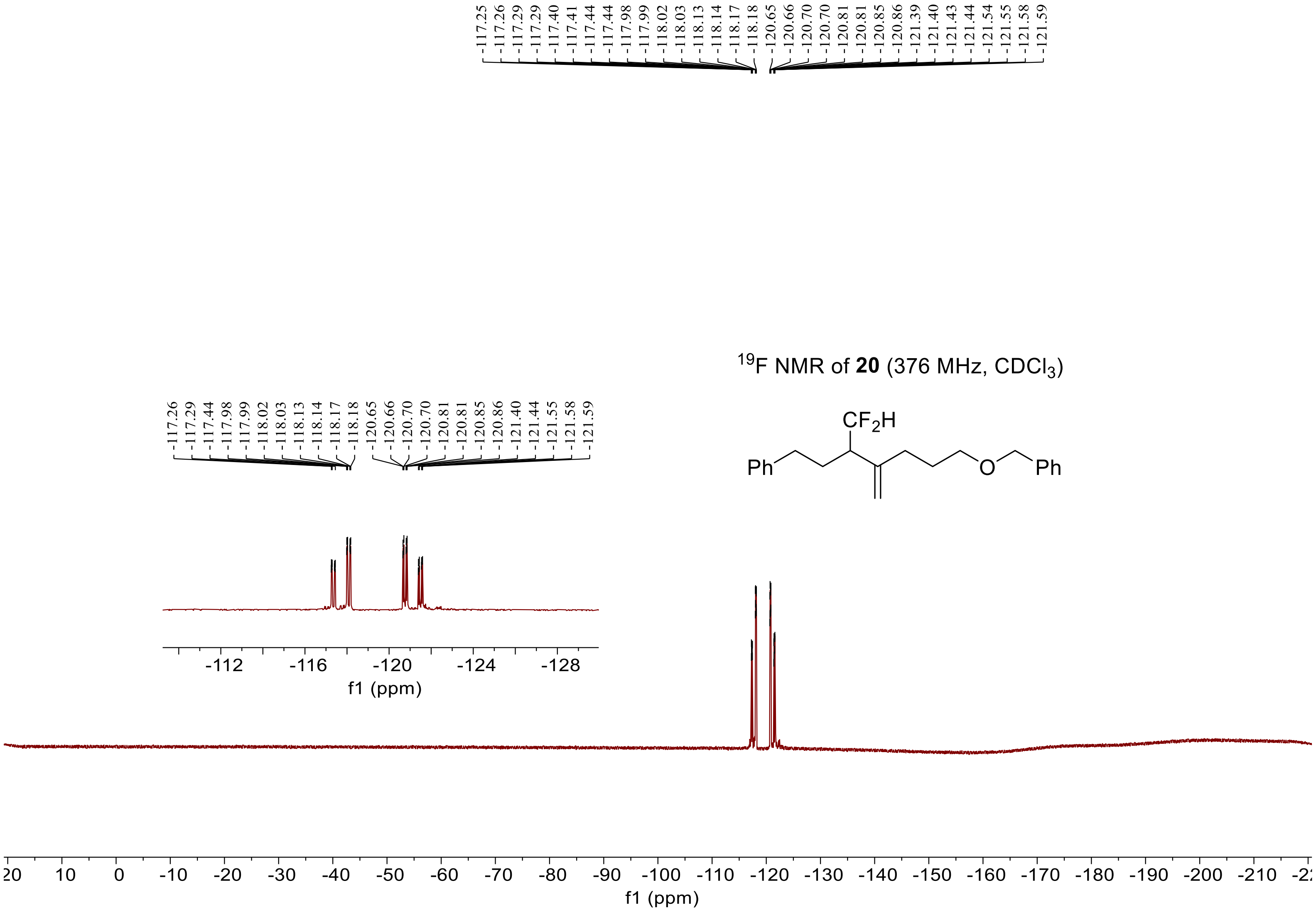
^{19}F NMR of **19** (376 MHz, $CDCl_3$)



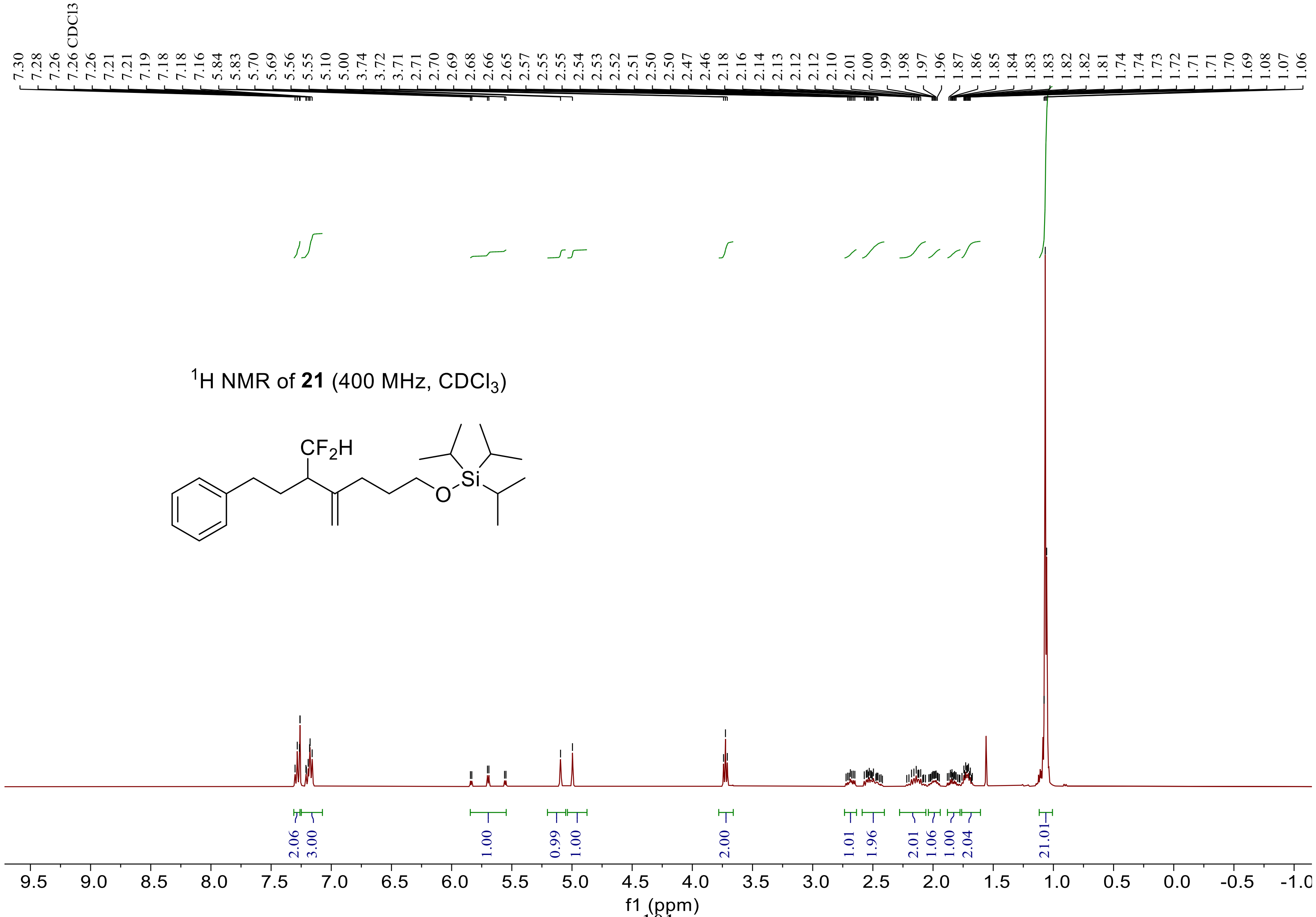
^{1}H NMR of **20** (400 MHz, $CDCl_3$)



^{13}C NMR of **20** (101 MHz, $CDCl_3$)

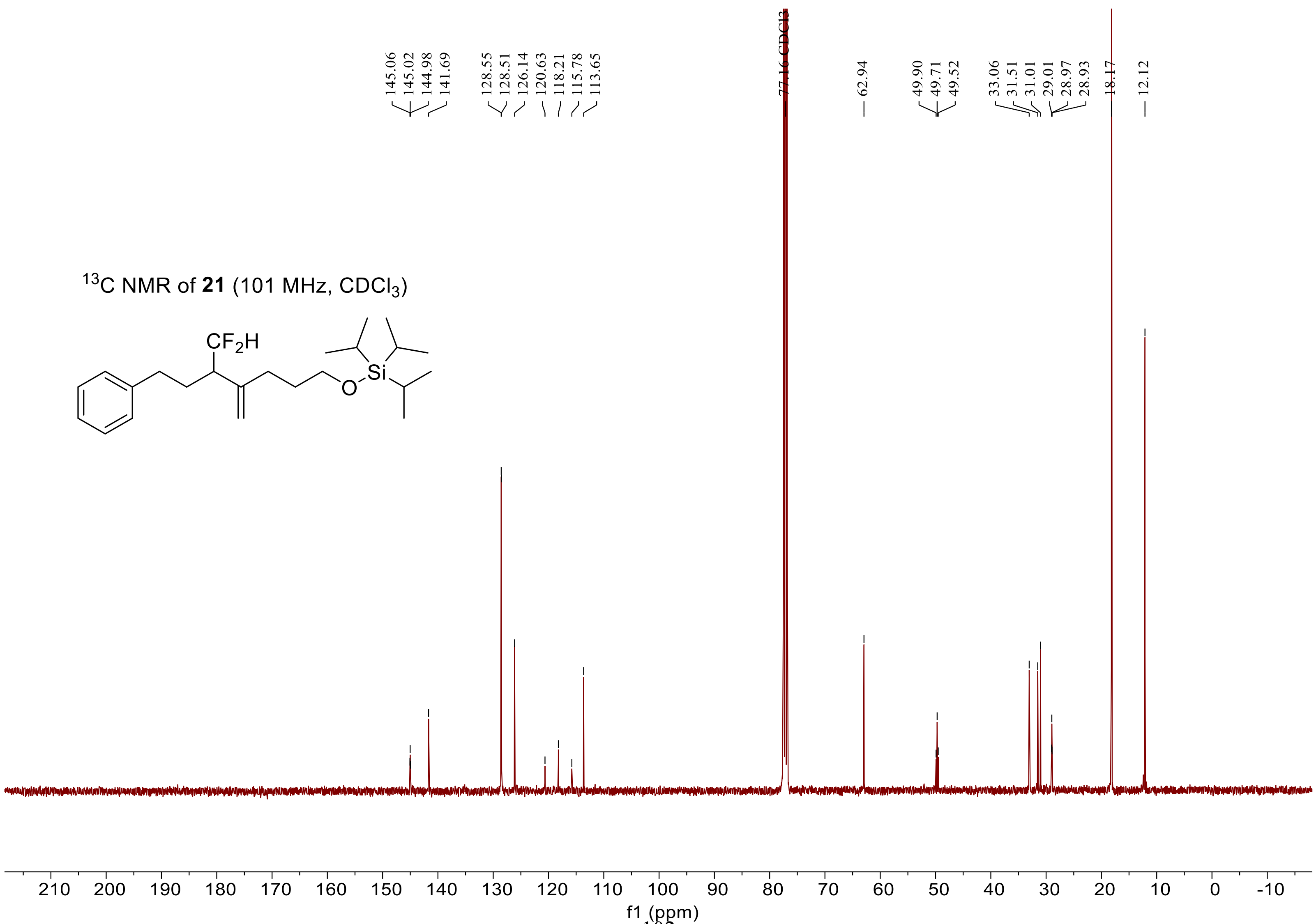


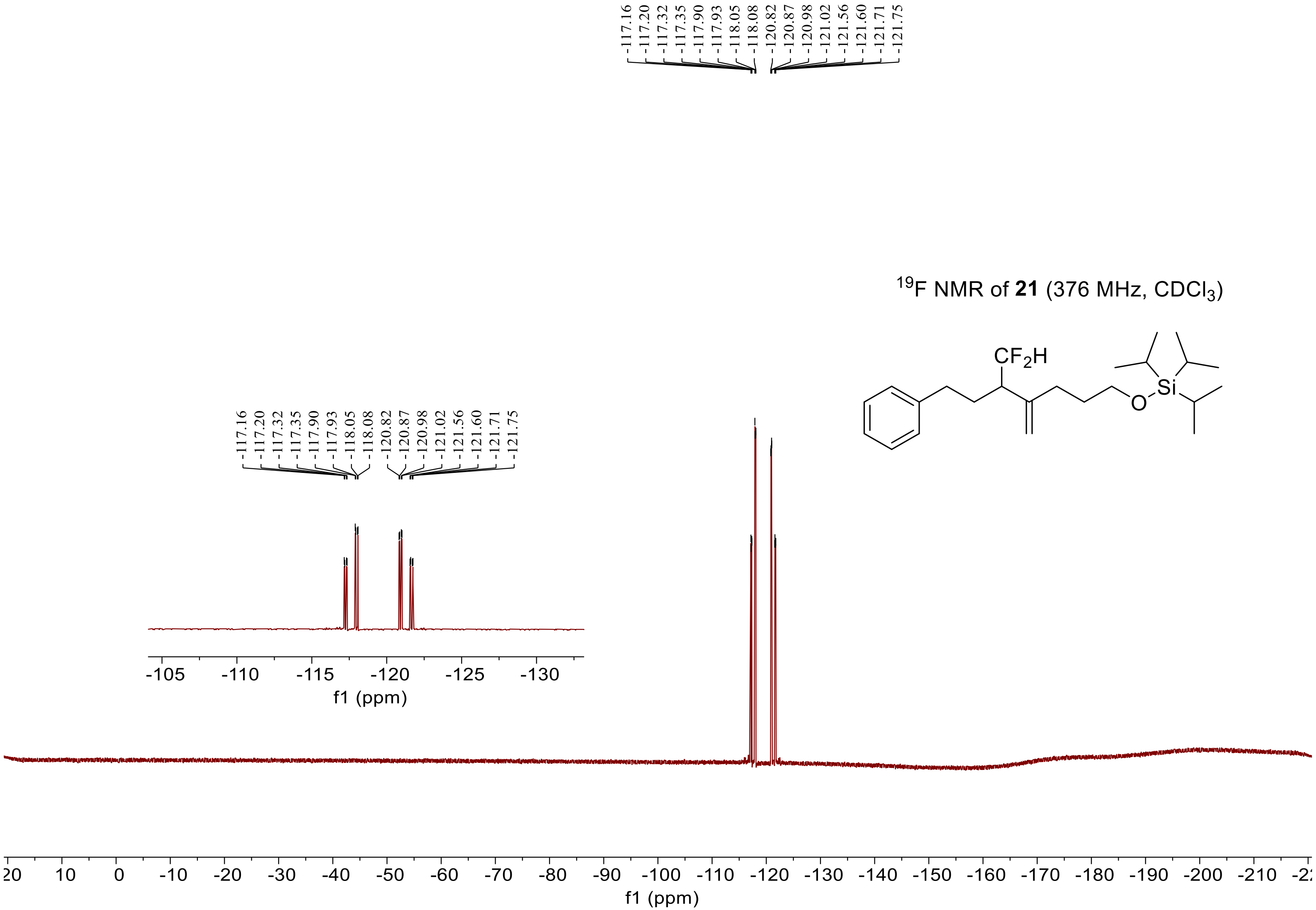
^{19}F NMR of **20** (376 MHz, $CDCl_3$)



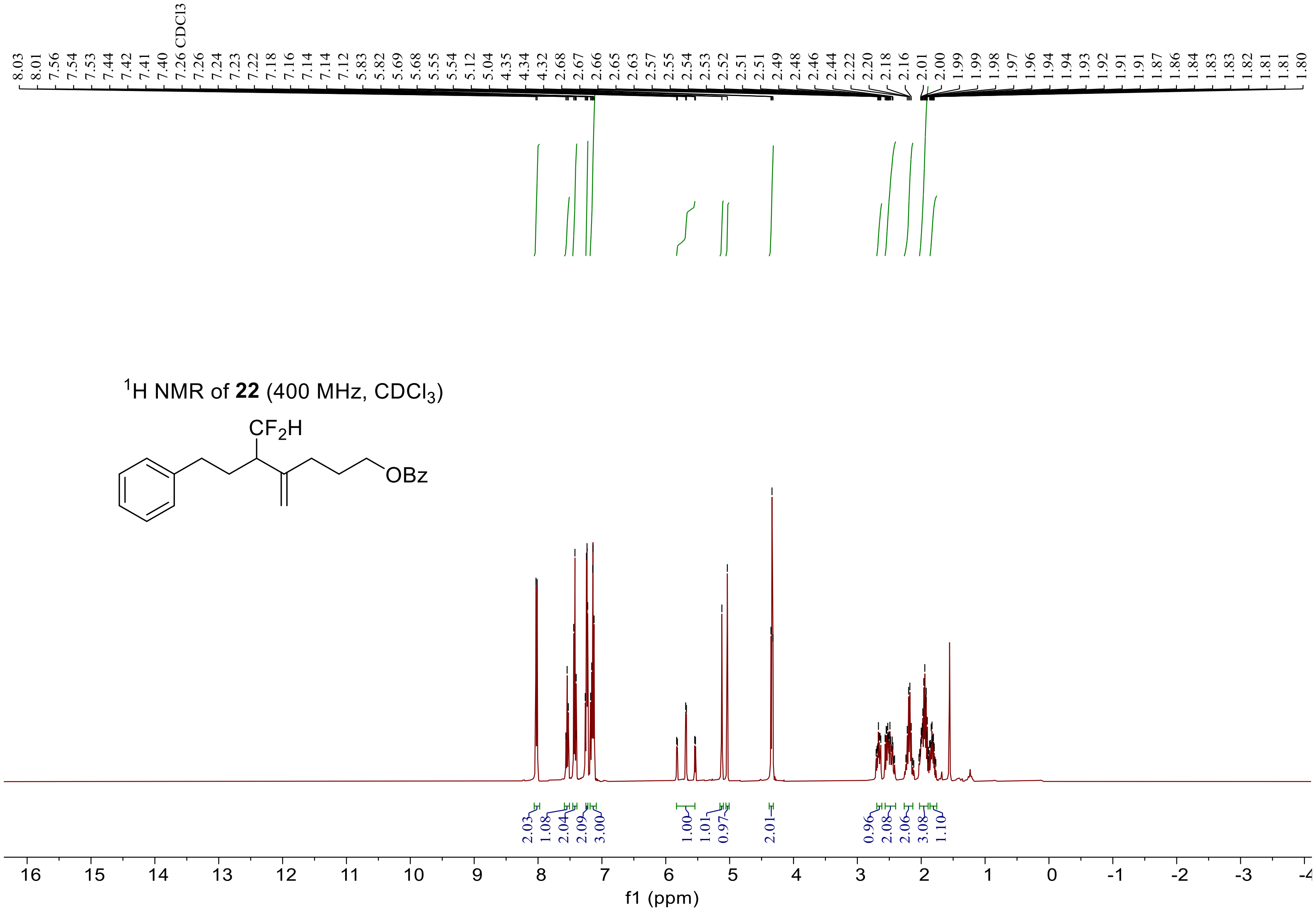
[1]H NMR of **21** (400 MHz, $CDCl_3$)

^{13}C NMR of **21** (101 MHz, $CDCl_3$)

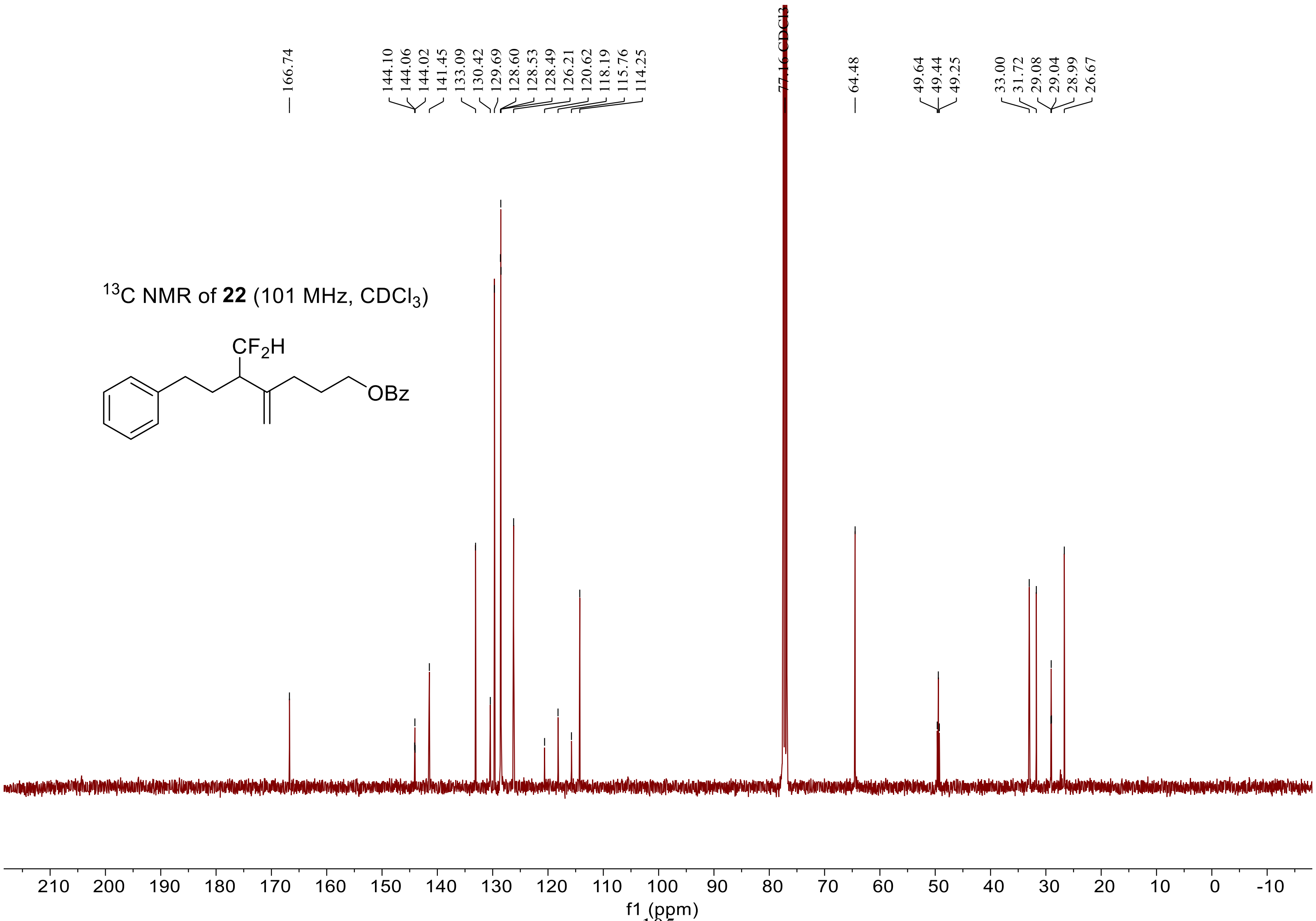


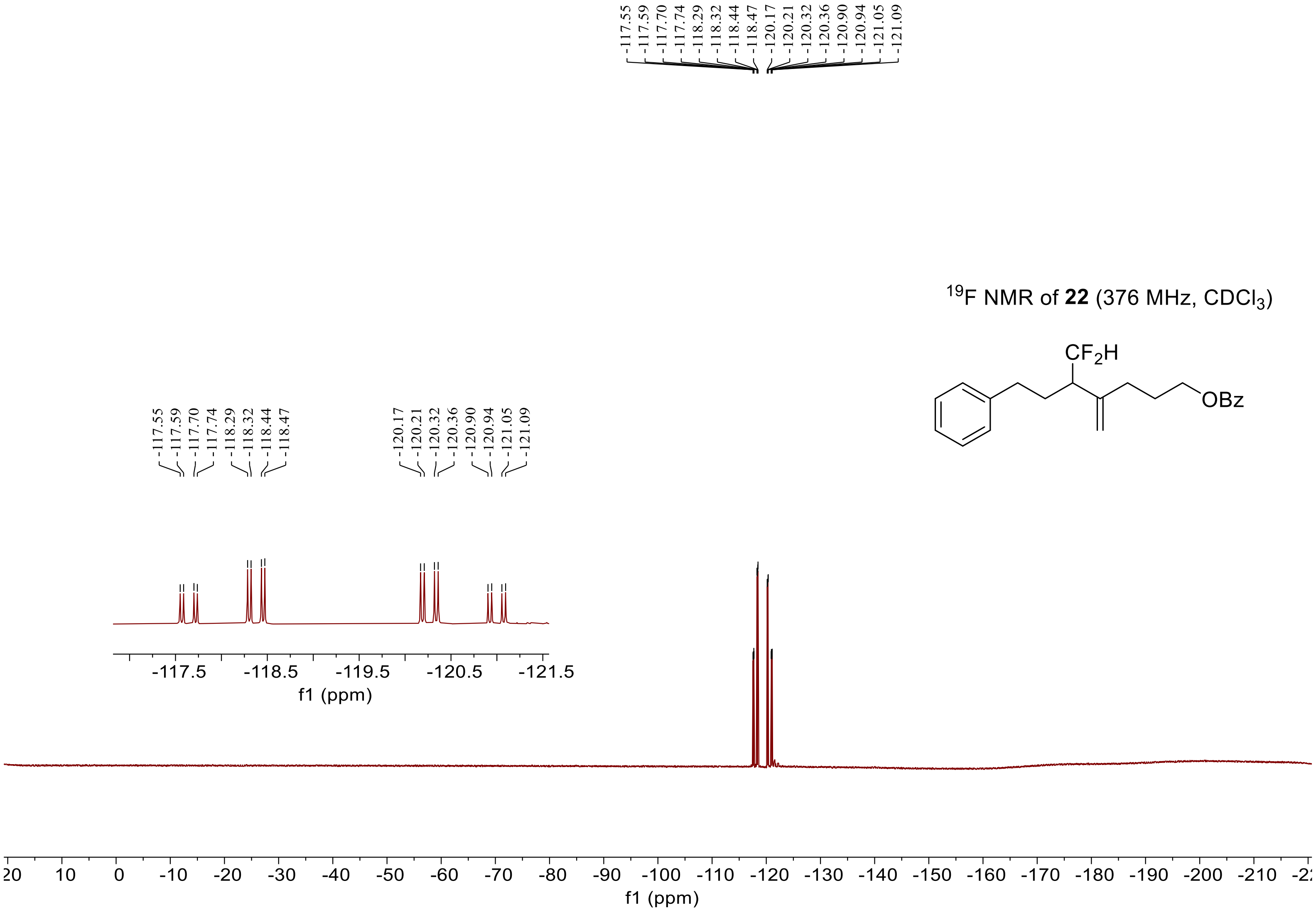

-117.16
-117.20
-117.32
-117.35
-117.90
-117.93
-118.05
-118.08
-120.82
-120.87
-120.98
-121.02
-121.56
-121.60
-121.71
-121.75
^{19}F NMR of **21** (376 MHz, $CDCl_3$)
CF2H
O
Si
-105
-110
-115
-120
-125
-130
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

[1]H NMR of **22** (400 MHz, $CDCl_3$)

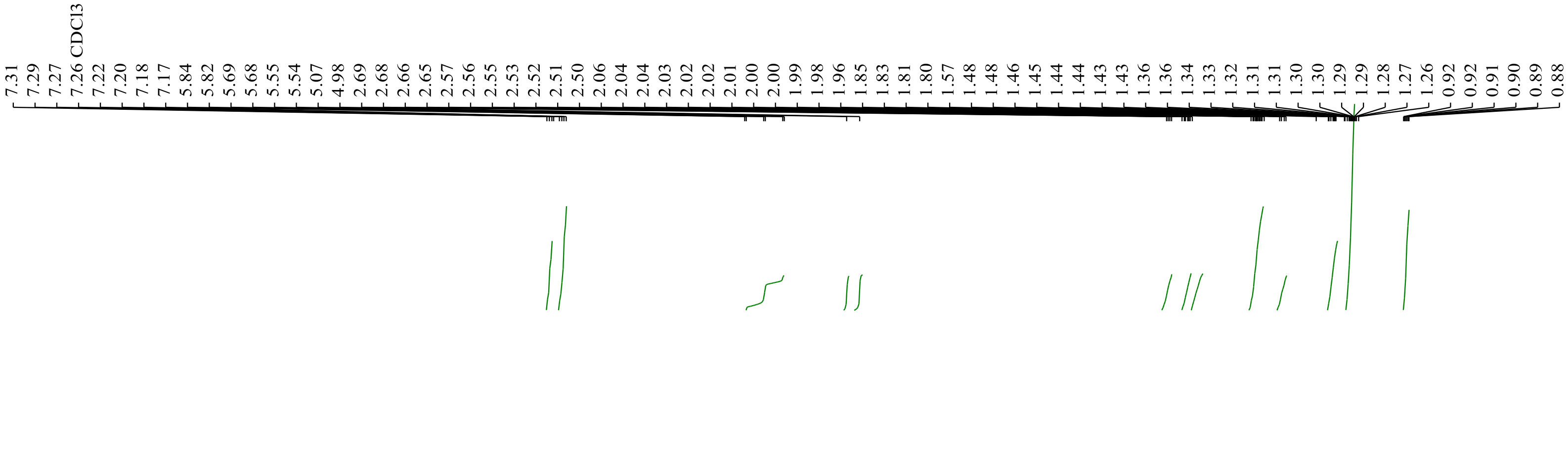


^{13}C NMR of **22** (101 MHz, $CDCl_3$)

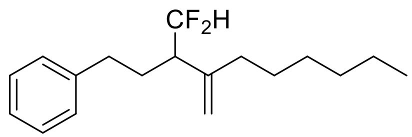


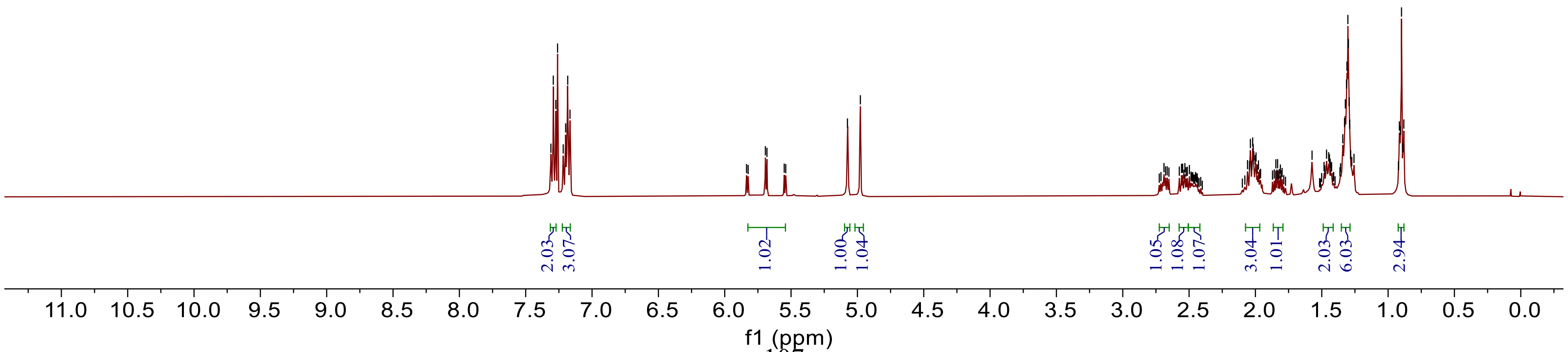


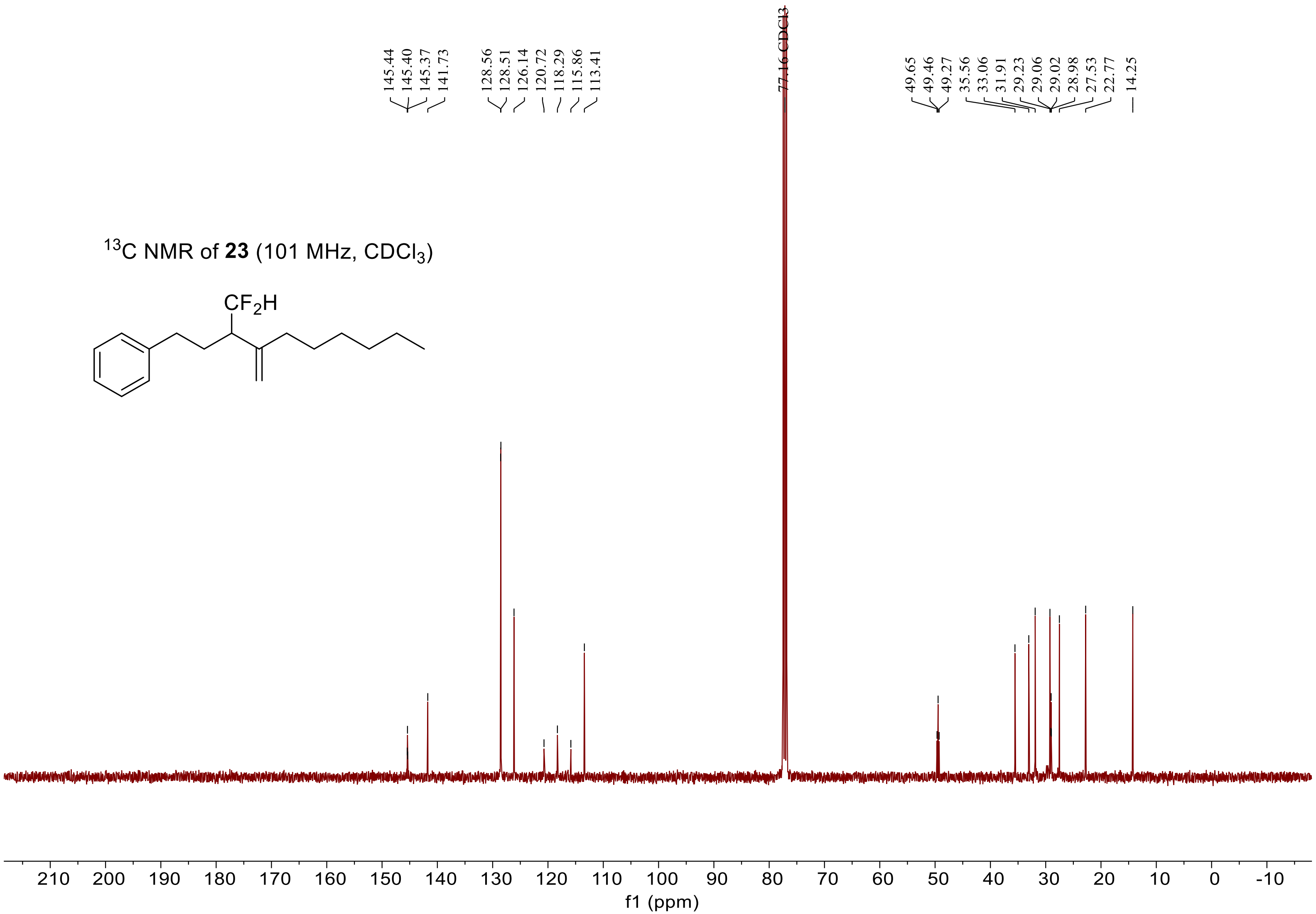
-117.55
-117.59
-117.70
-117.74
-118.29
-118.32
-118.44
-118.47
-120.17
-120.21
-120.32
-120.36
-120.90
-120.94
-121.05
-121.09
^{19}F NMR of **22** (376 MHz, $CDCl_3$)
CF_2H
OBz
-117.5
-118.5
-119.5
-120.5
-121.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



^1H NMR of **23** (400 MHz, $CDCl_3$)

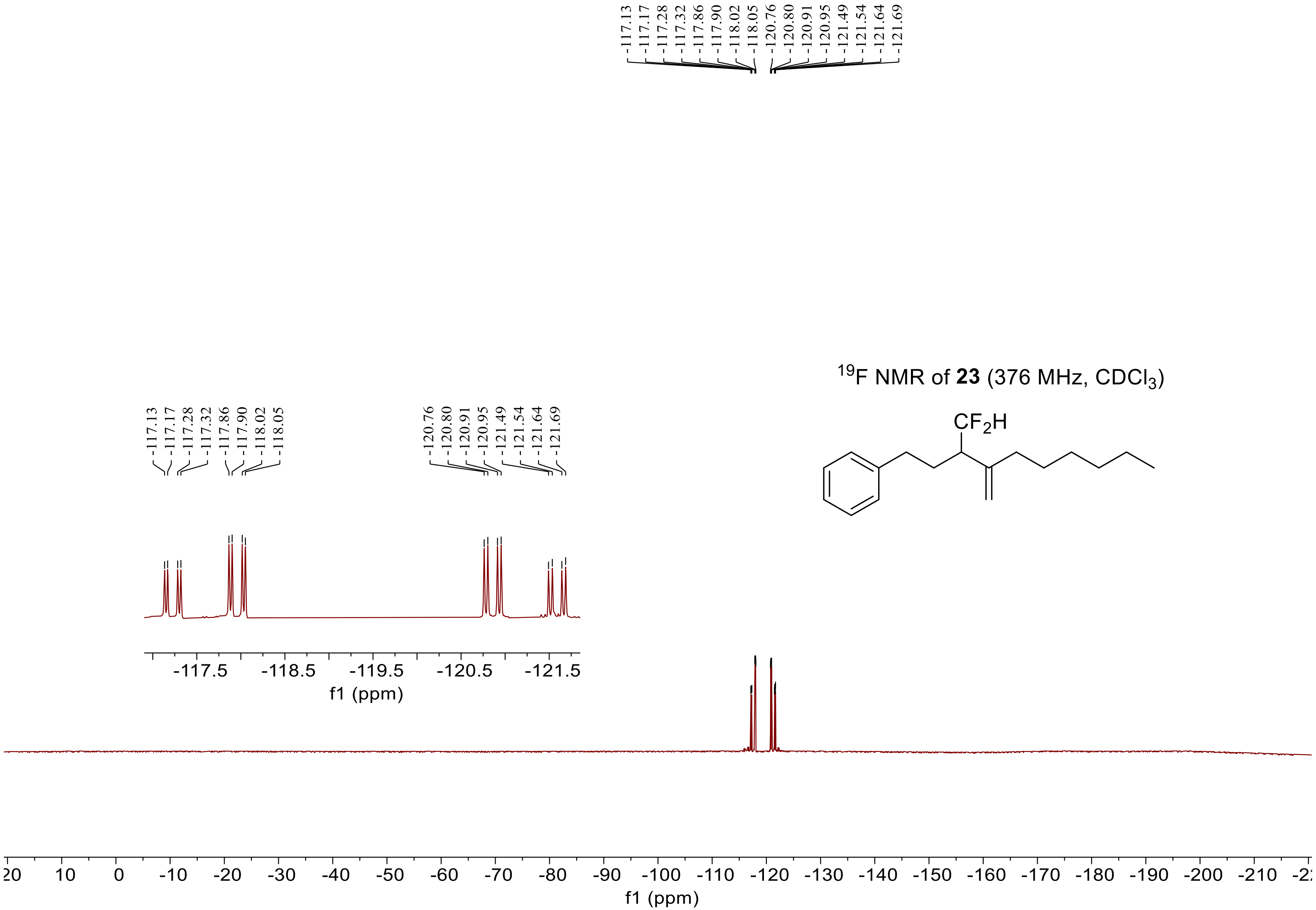


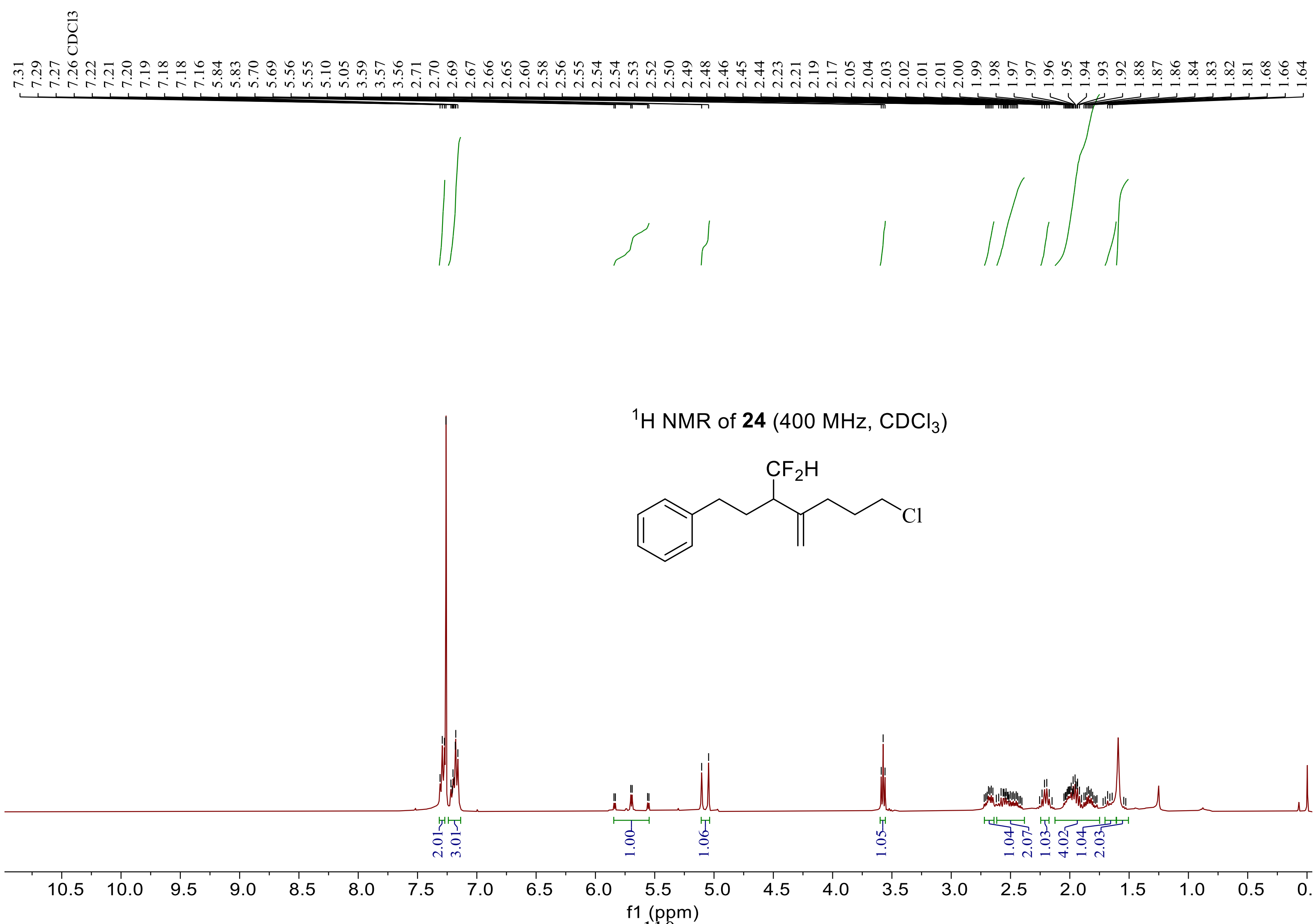




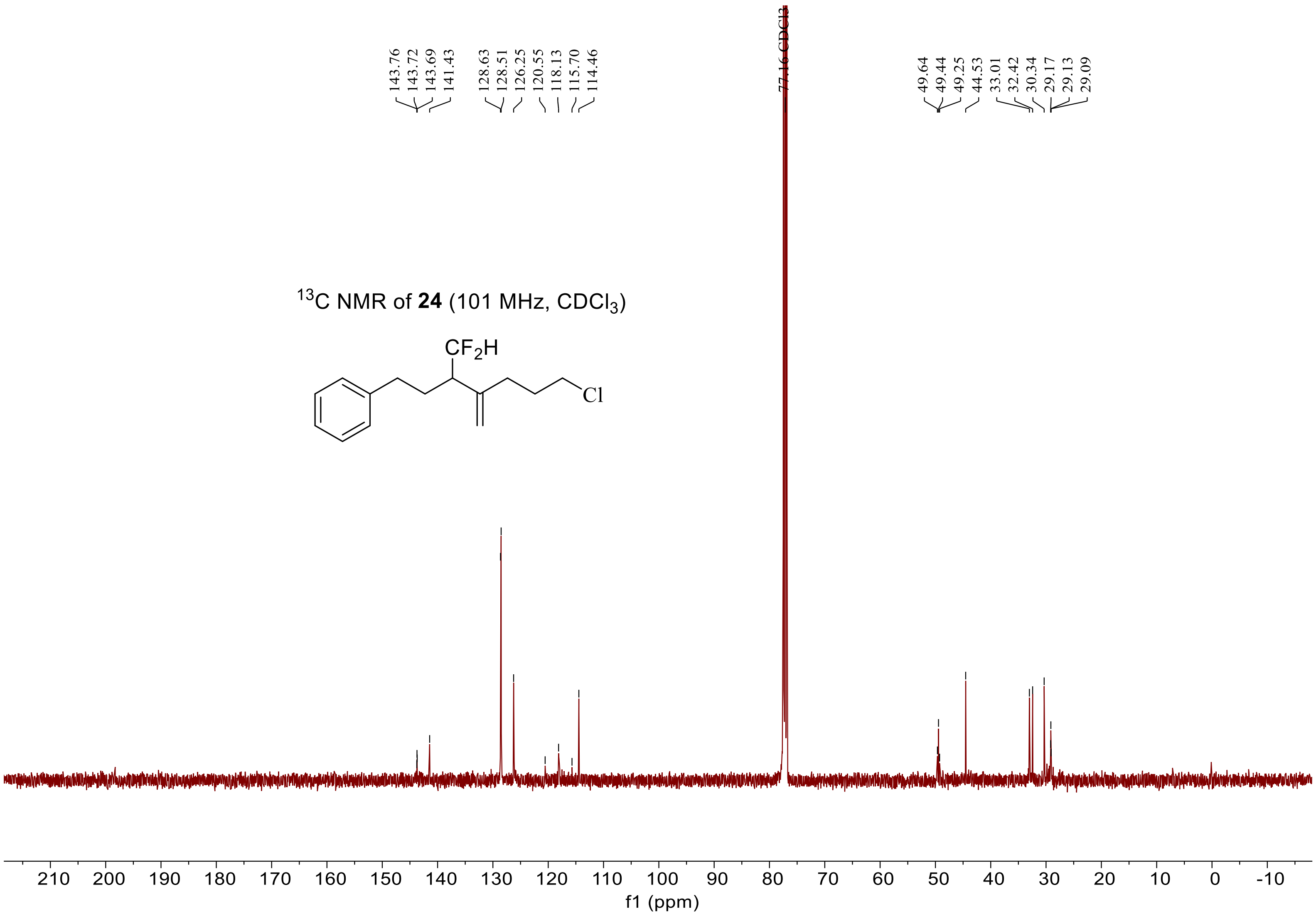
^{13}C NMR of **23** (101 MHz, $CDCl_3$)
CF_2H
145.44
145.40
145.37
141.73
128.56
128.51
126.14
120.72
118.29
115.86
113.41
77.16 CDCl3
49.65
49.46
49.27
35.56
33.06
31.91
29.23
29.06
29.02
28.98
27.53
22.77
14.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

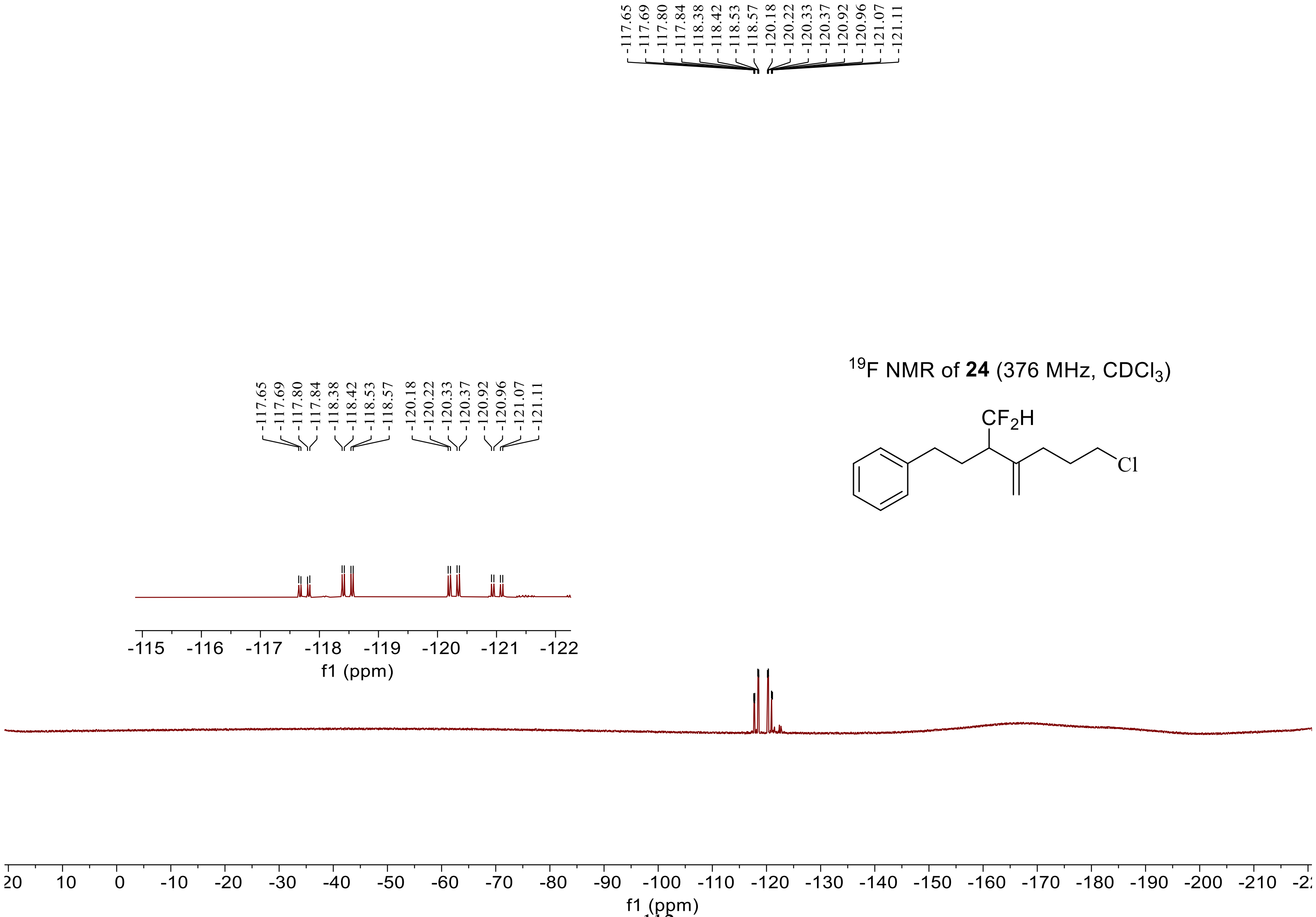
^{19}F NMR of **23** (376 MHz, $CDCl_3$)





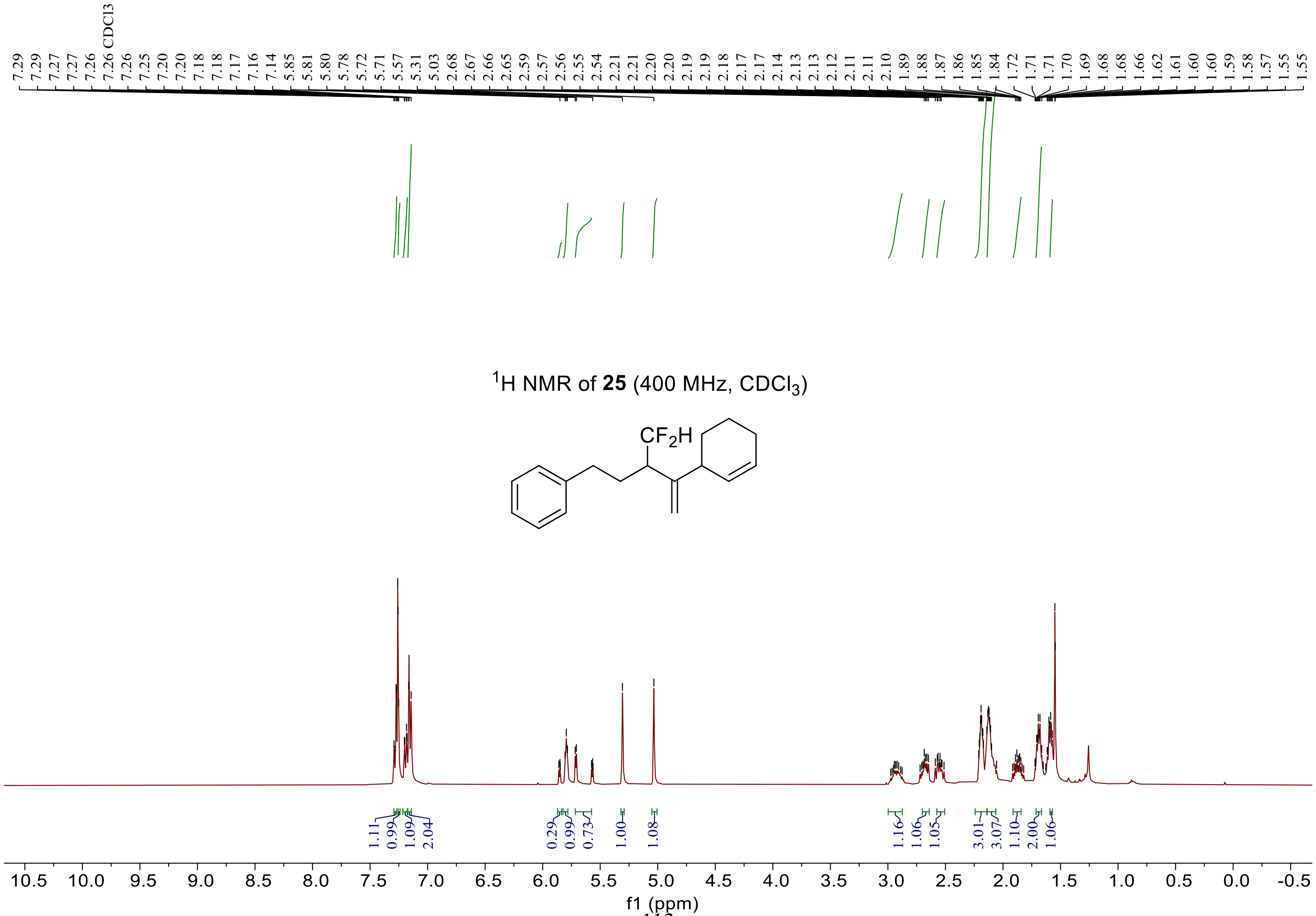
^{1}H NMR of **24** (400 MHz, CDCl$_3$)
CF$_2$H
Cl
f1 (ppm)

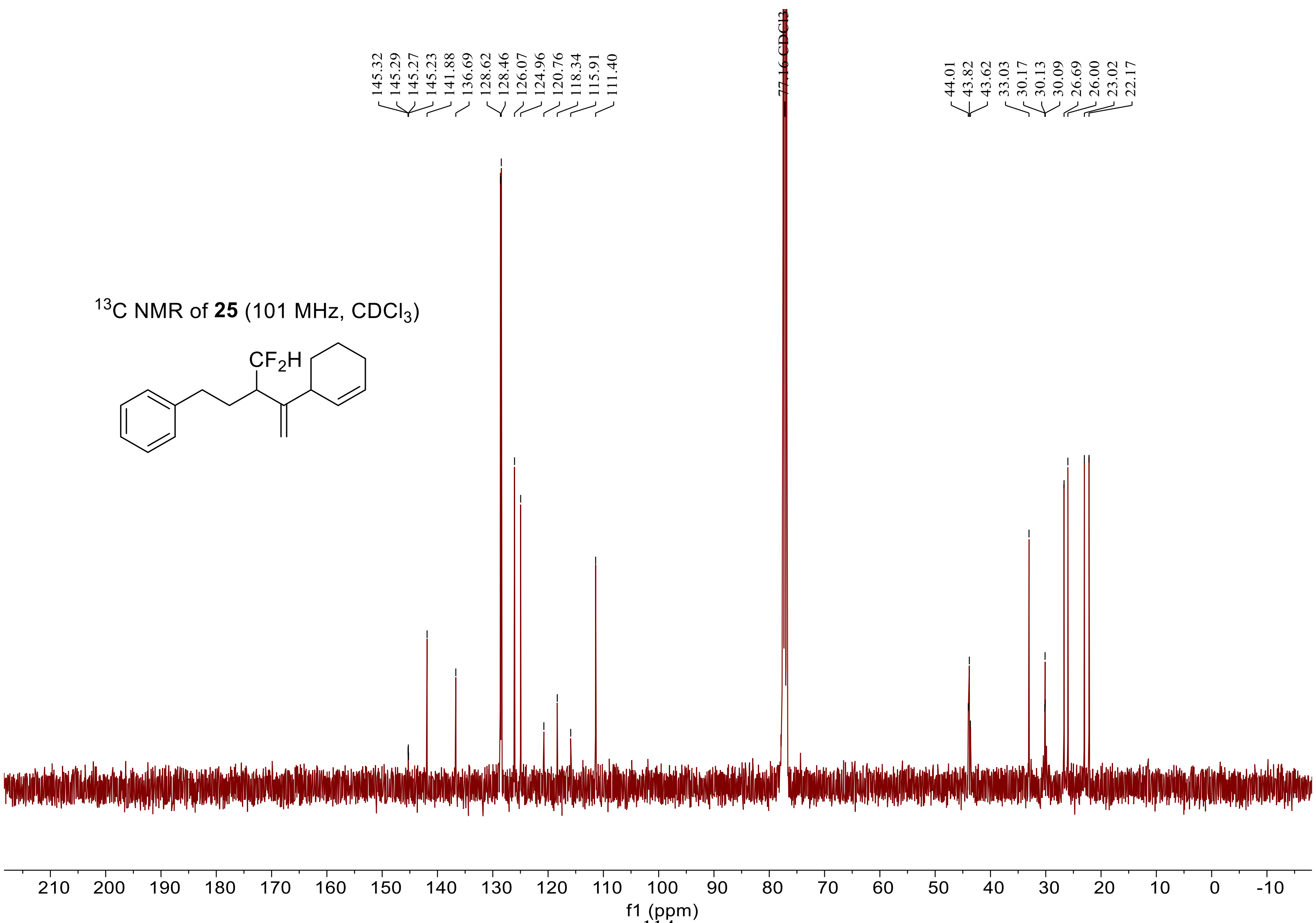




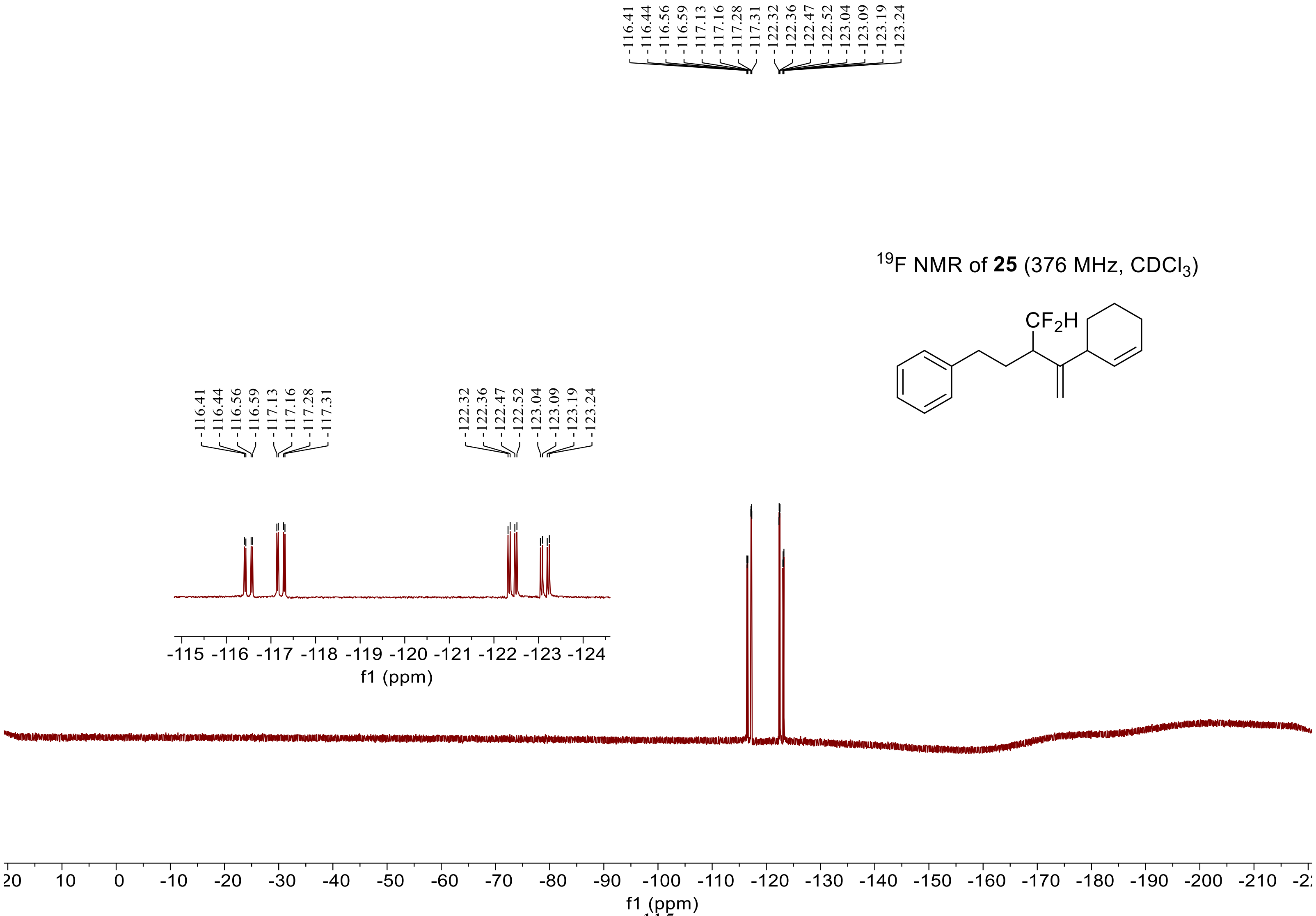
^{19}F NMR of **24** (376 MHz, $CDCl_3$)

^{1}H NMR of **25** (400 MHz, $CDCl_3$)

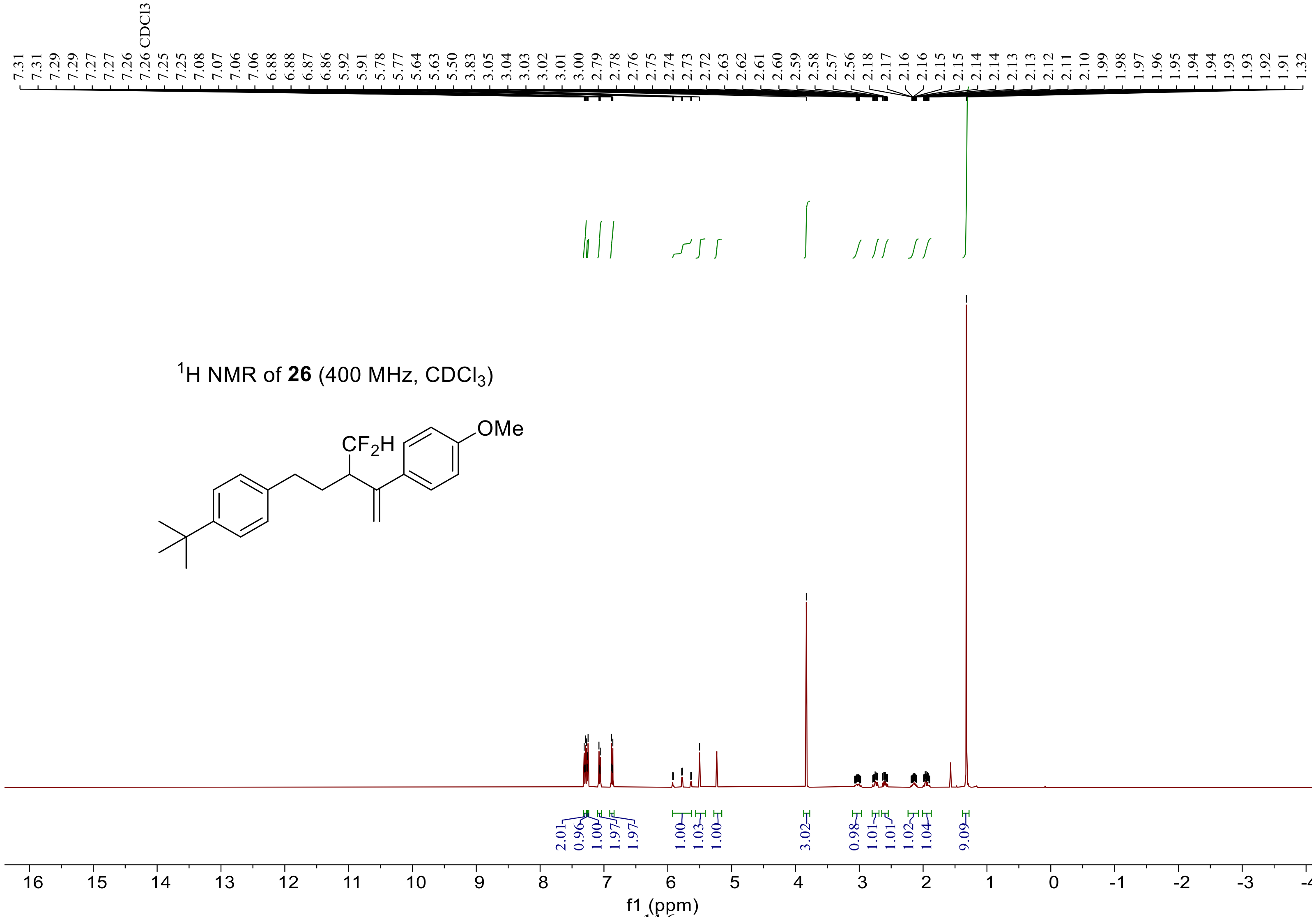




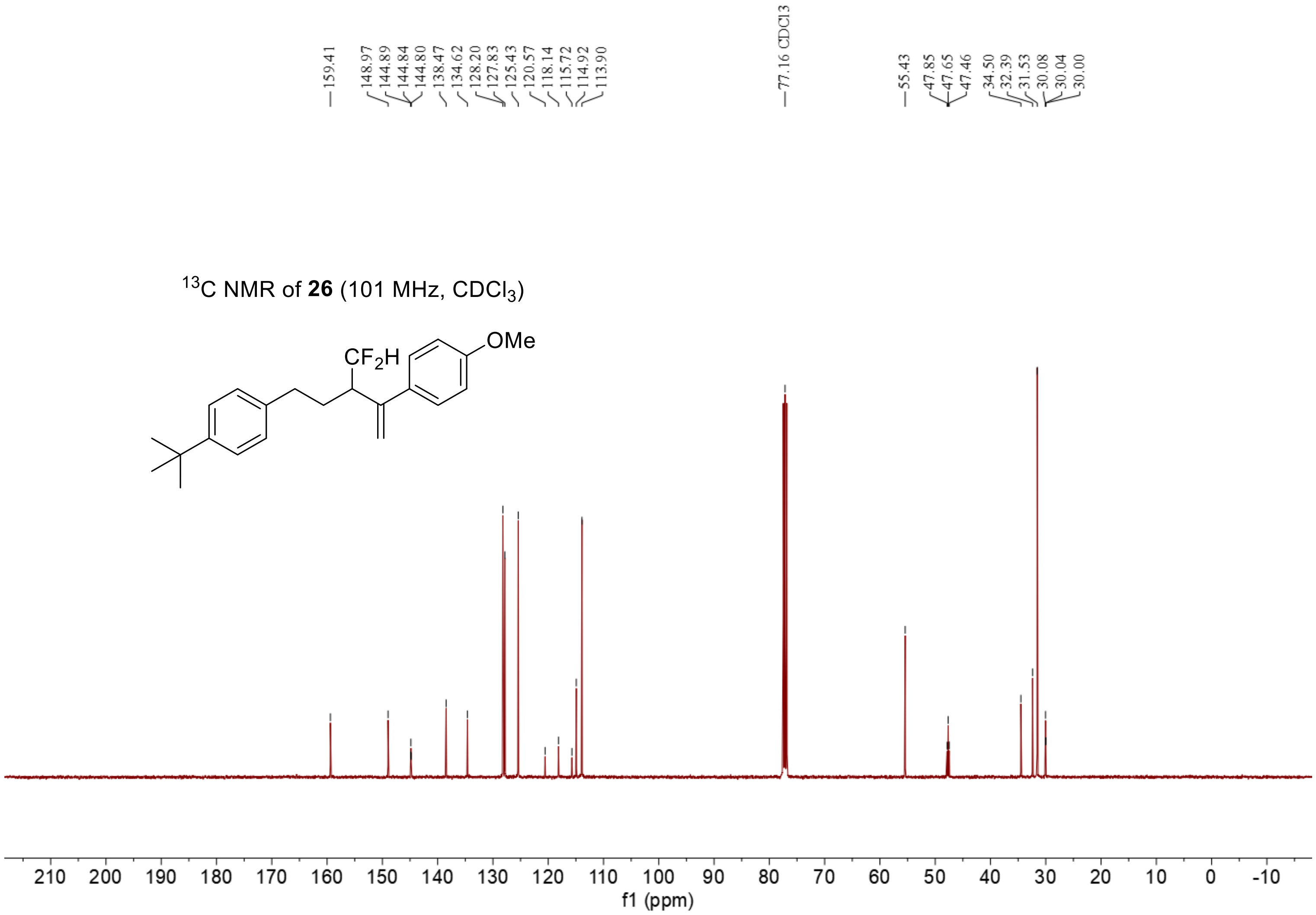
145.32
145.29
145.27
145.23
141.88
136.69
128.62
128.46
126.07
124.96
120.76
118.34
115.91
111.40
77.16 CDCl3
44.01
43.82
43.62
33.03
30.17
30.13
30.09
26.69
26.00
23.02
22.17
^{13}C NMR of **25** (101 MHz, $CDCl_3$)
CF_2H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

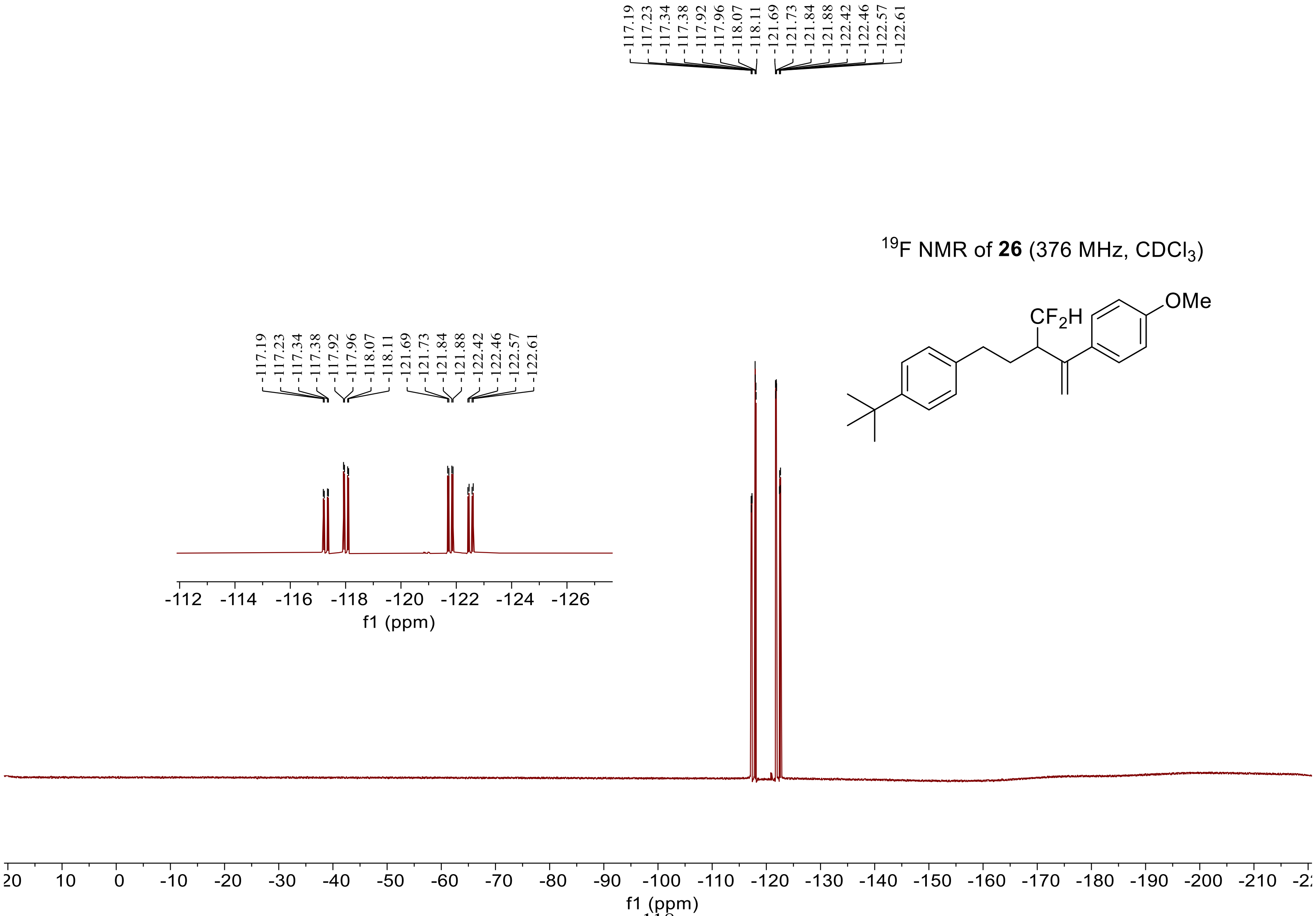


^{19}F NMR of **25** (376 MHz, $CDCl_3$)


7.31 7.31 7.29 7.29 7.27 7.27 7.26 7.26 CDCl3 7.25 7.25 7.08 7.07 7.06 7.06 6.88 6.88 6.87 6.86 5.92 5.91 5.78 5.77 5.64 5.63 5.50 3.83 3.05 3.04 3.03 3.02 3.01 3.00 2.79 2.78 2.76 2.75 2.74 2.73 2.72 2.63 2.62 2.61 2.60 2.59 2.58 2.57 2.56 2.18 2.17 2.16 2.16 2.15 2.15 2.14 2.14 2.13 2.13 2.12 2.11 2.10 1.99 1.98 1.97 1.96 1.95 1.94 1.94 1.93 1.93 1.92 1.91 1.32
^{1}H NMR of **26** (400 MHz, $CDCl_3$)
CF2H
OMe
2.01 0.96 1.00 1.97 1.97 1.00 1.03 1.00 3.02 0.98 1.01 1.01 1.02 1.04 9.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

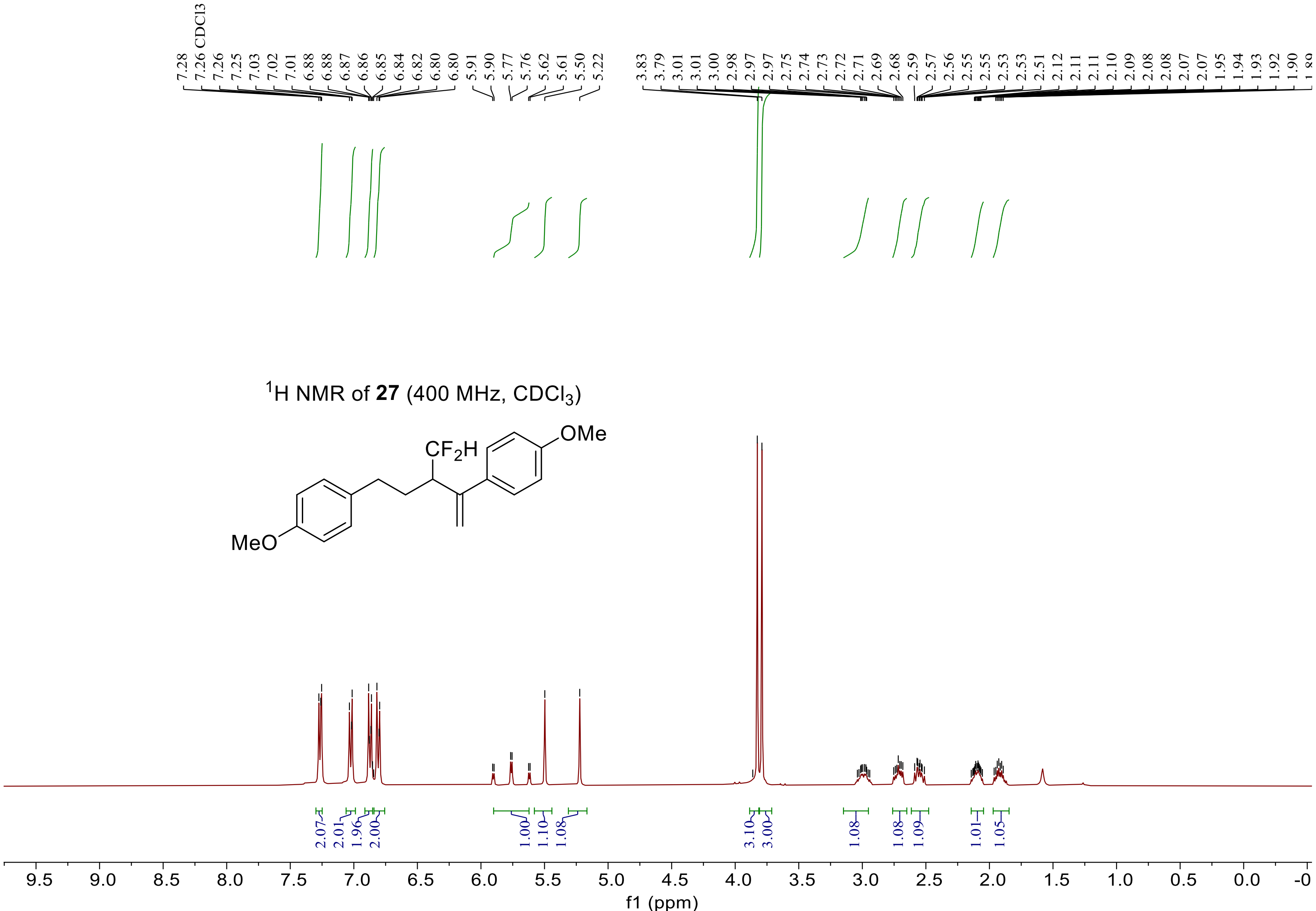
^{13}C NMR of **26** (101 MHz, $CDCl_3$)

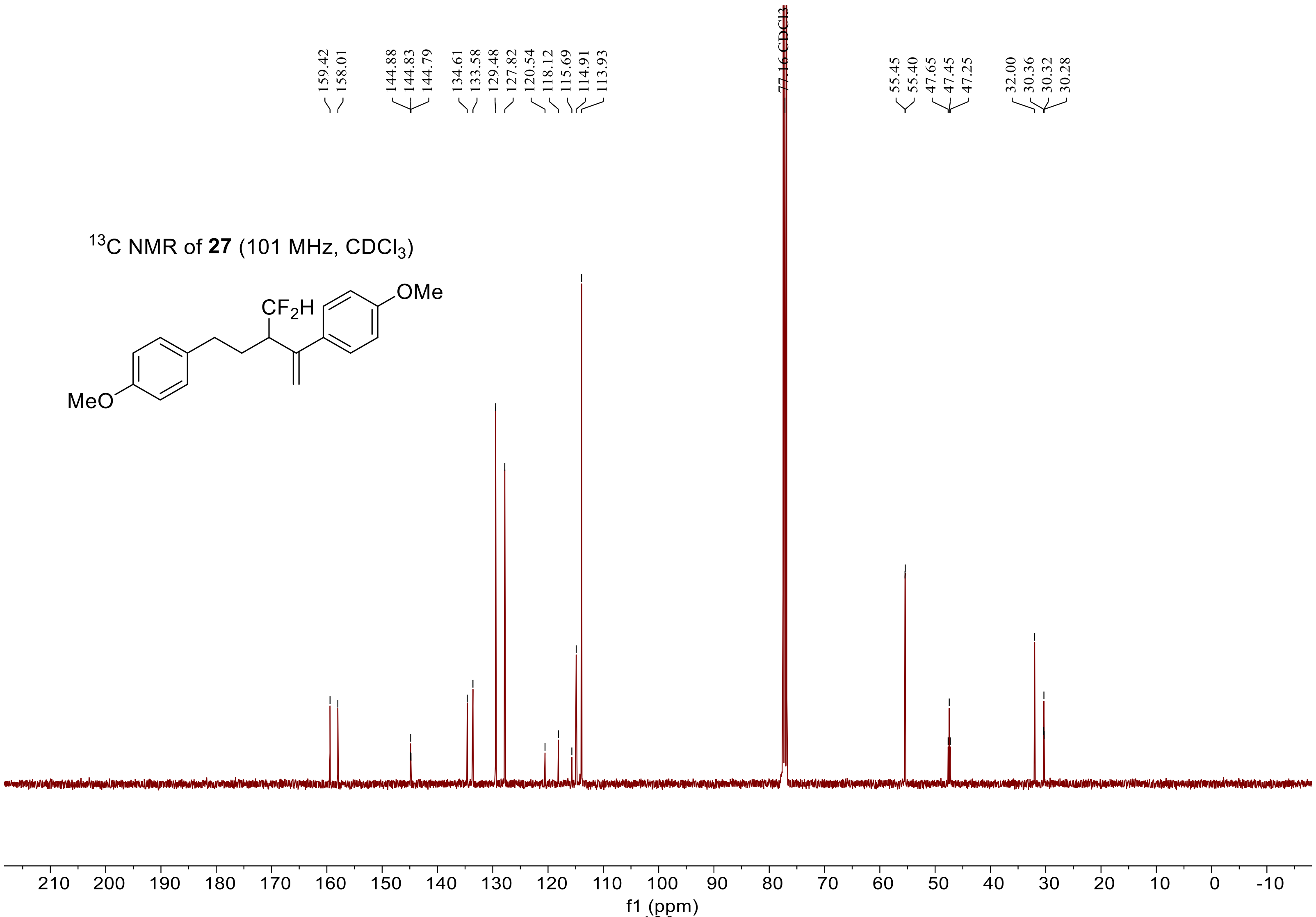




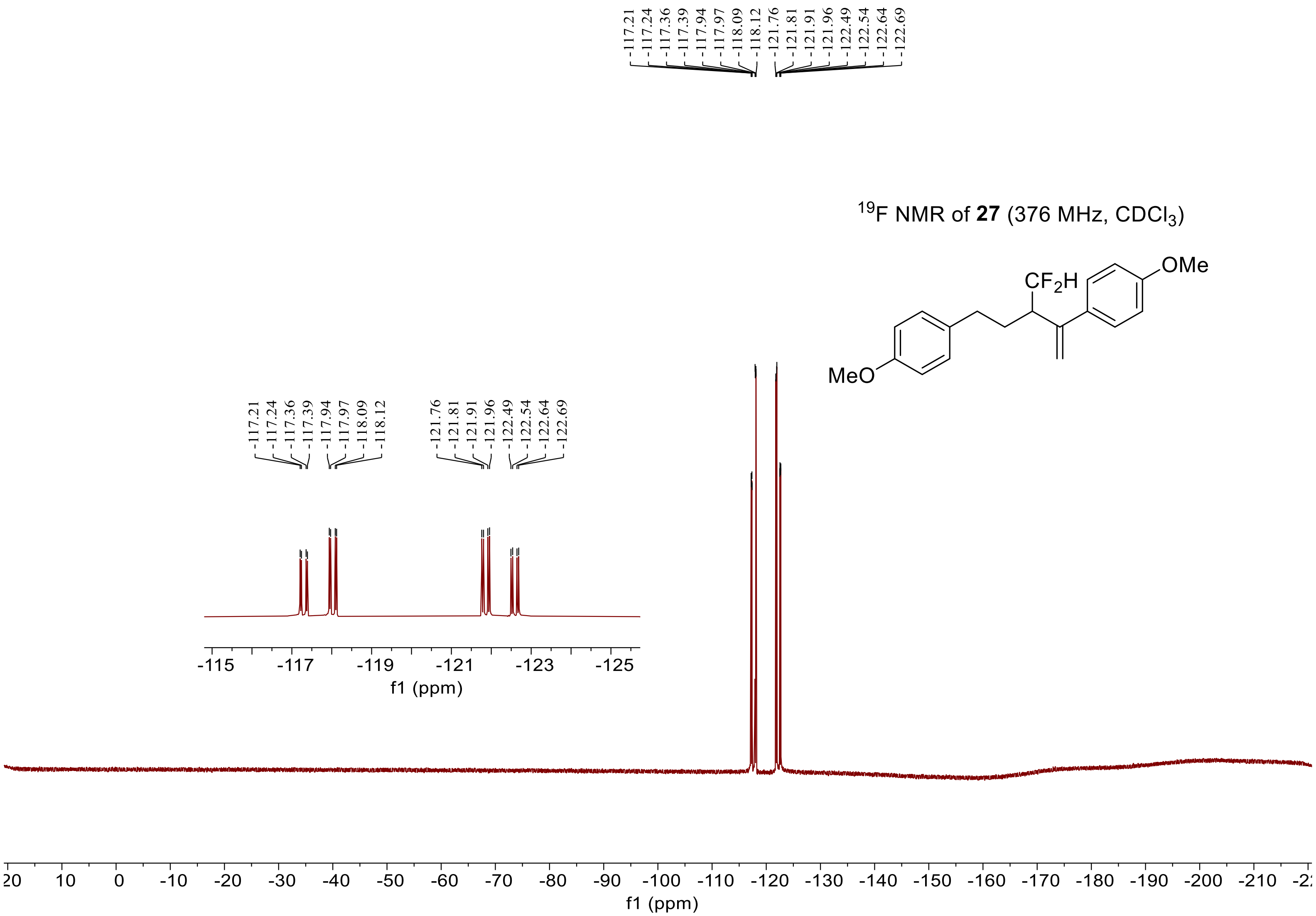
^{19}F NMR of **26** (376 MHz, $CDCl_3$)

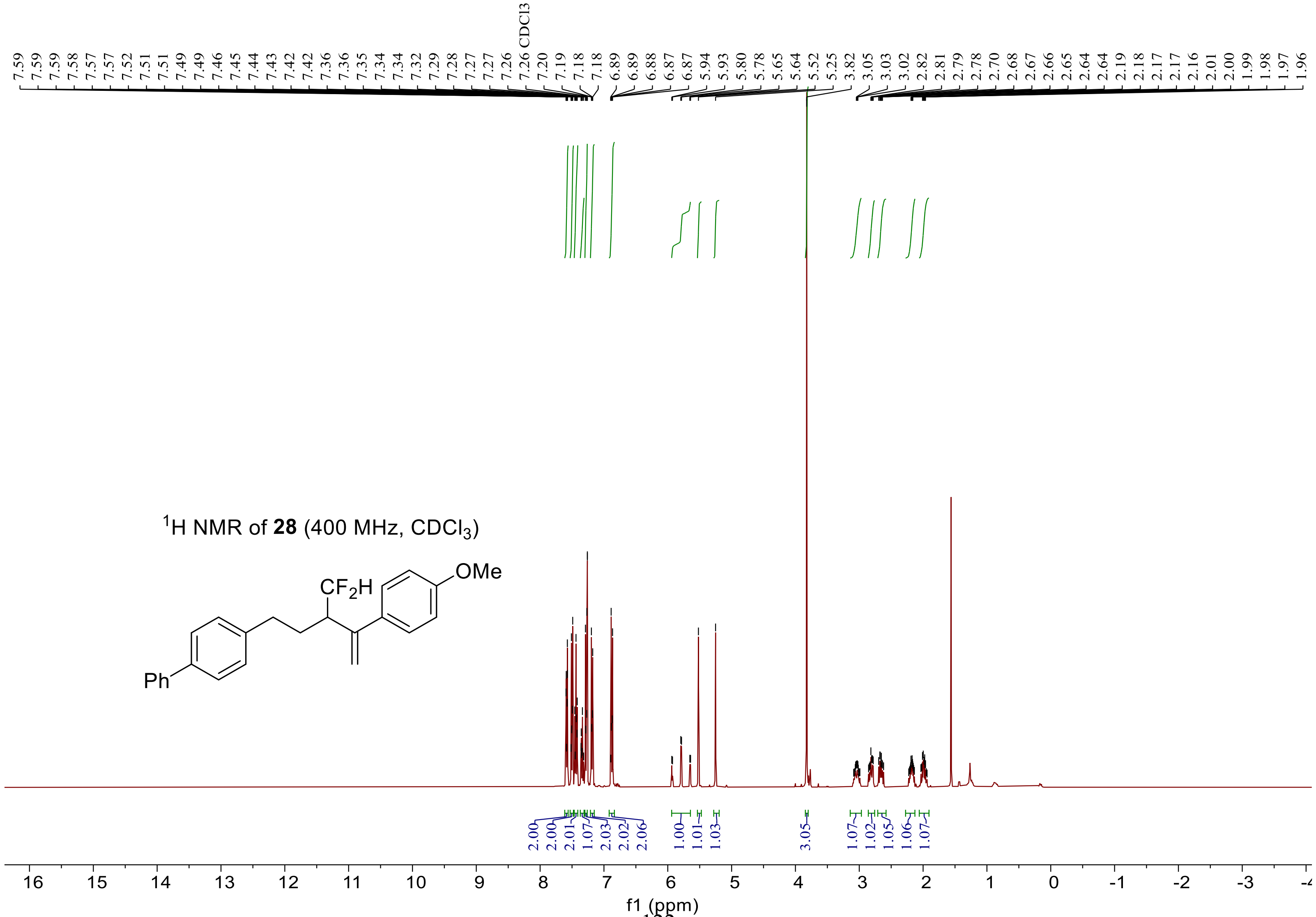
[1]H NMR of **27** (400 MHz, $CDCl_3$)




^{13}C NMR of **27** (101 MHz, $CDCl_3$)
CF_2H
OMe
MeO
159.42
158.01
144.88
144.83
144.79
134.61
133.58
129.48
127.82
120.54
118.12
115.69
114.91
113.93
77.16 CDCl3
55.45
55.40
47.65
47.45
47.25
32.00
30.36
30.32
30.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

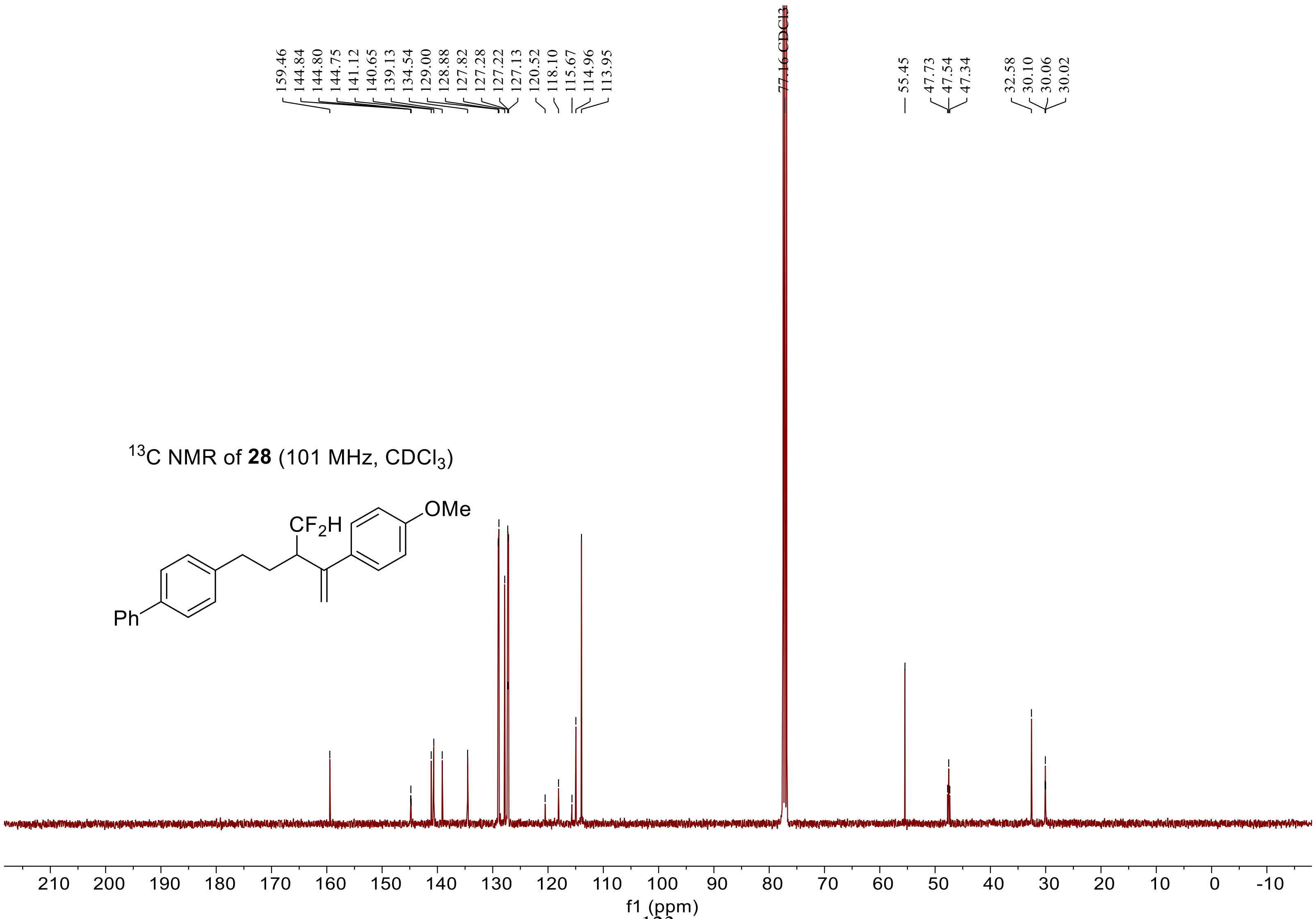
^{19}F NMR of **27** (376 MHz, $CDCl_3$)



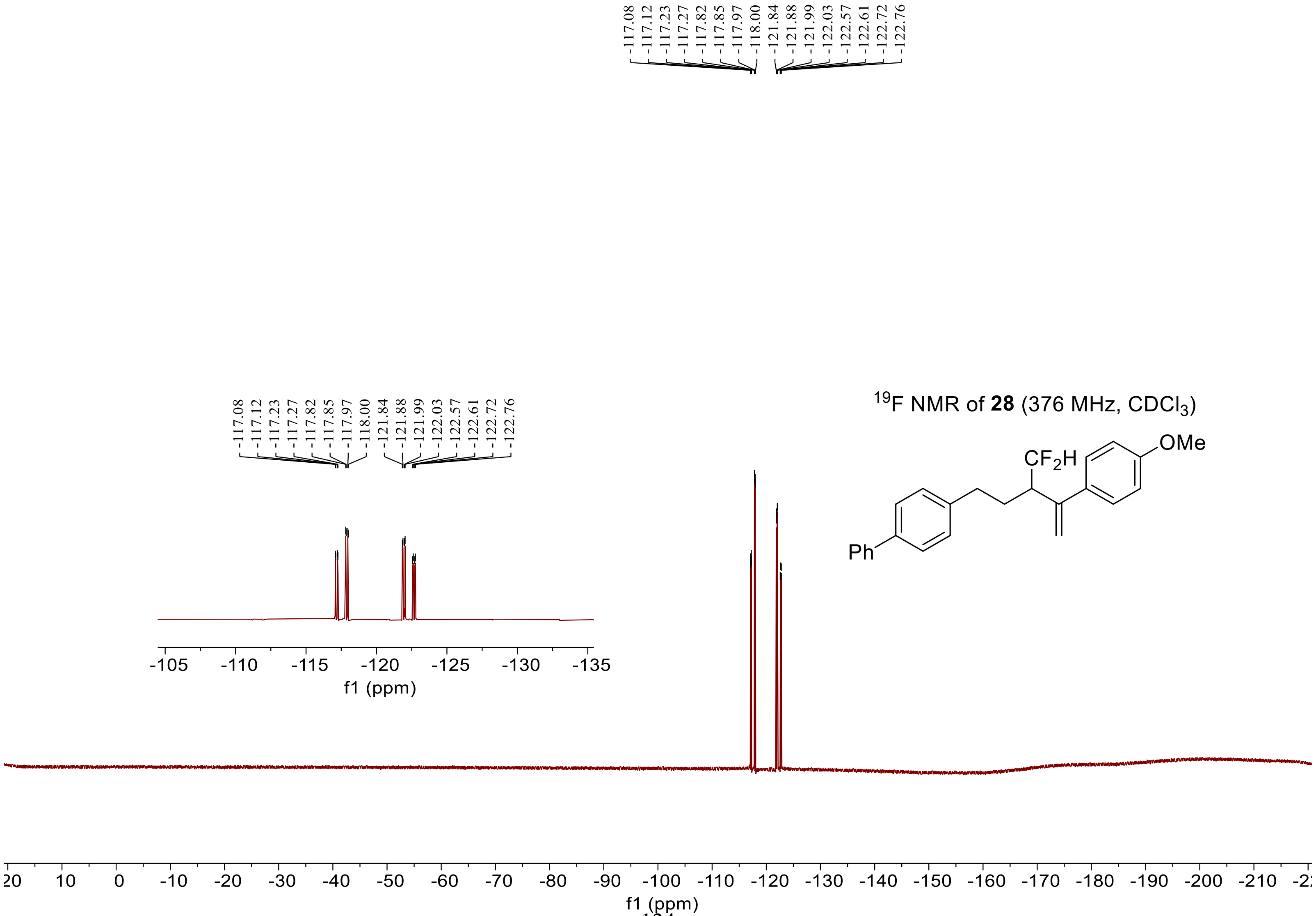


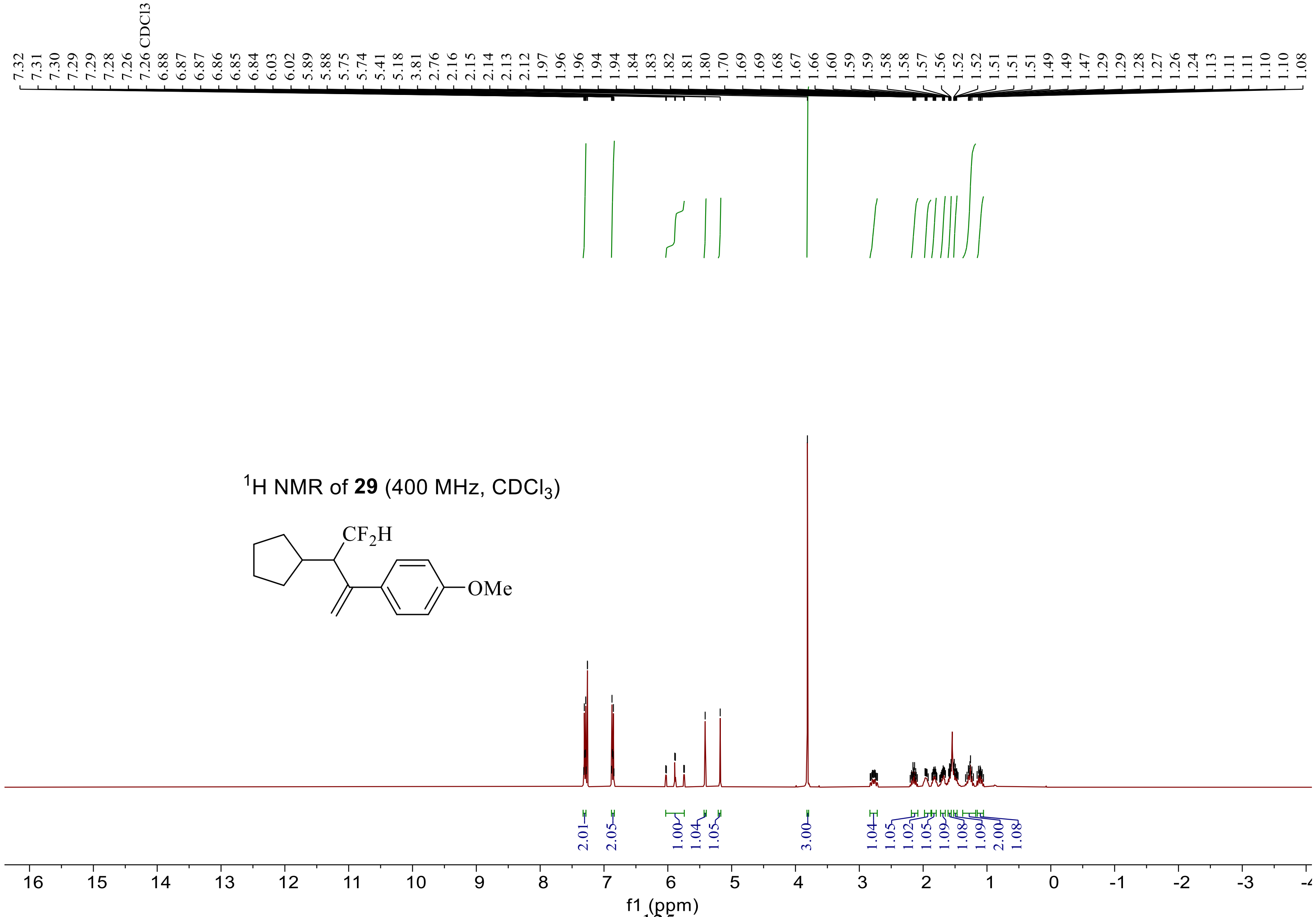
1H NMR of 28 (400 MHz, CDCl3)
OMe
CF2H
Ph
f1 (ppm)

^{13}C NMR of **28** (101 MHz, $CDCl_3$)



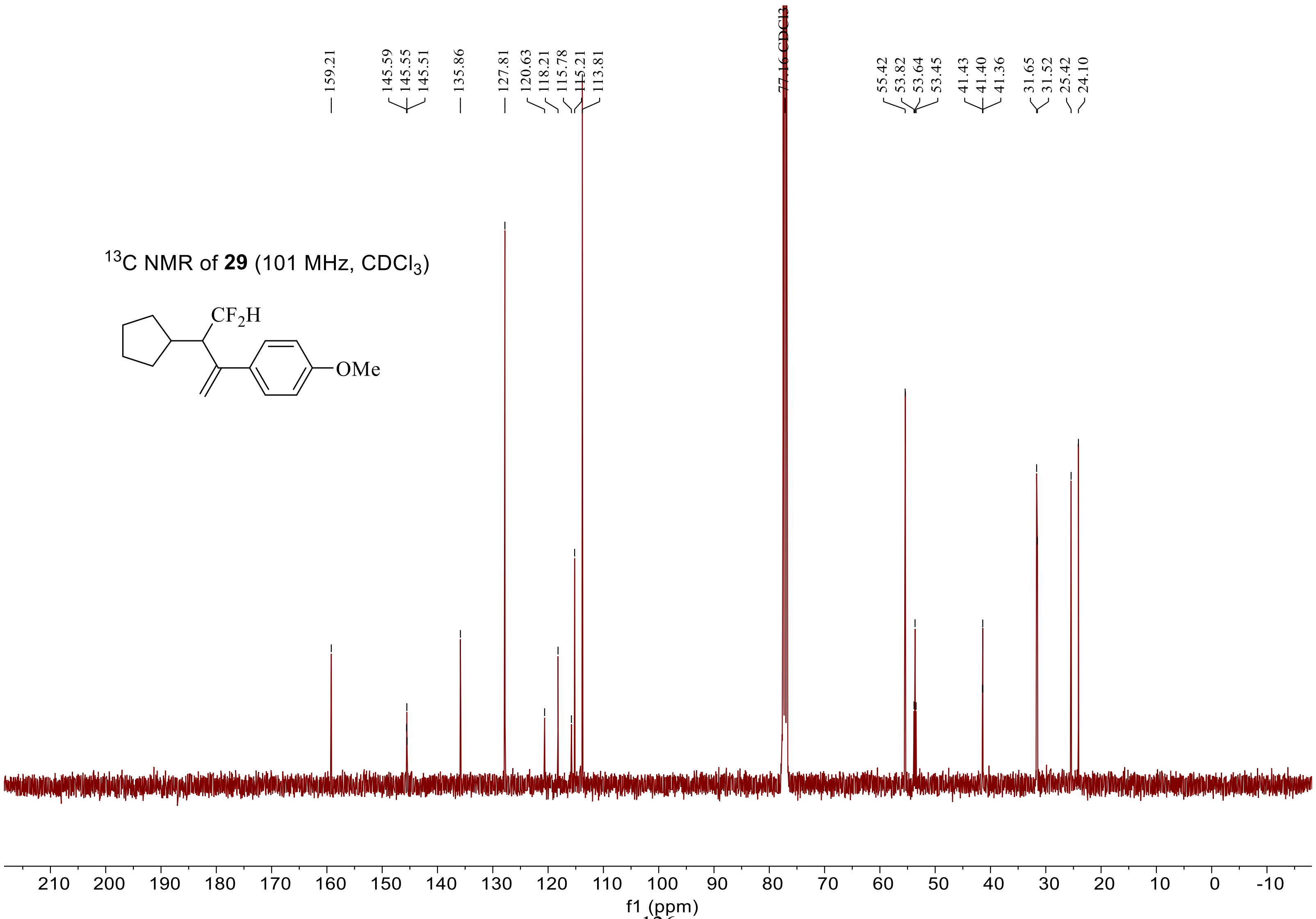
^{19}F NMR of **28** (376 MHz, $CDCl_3$)

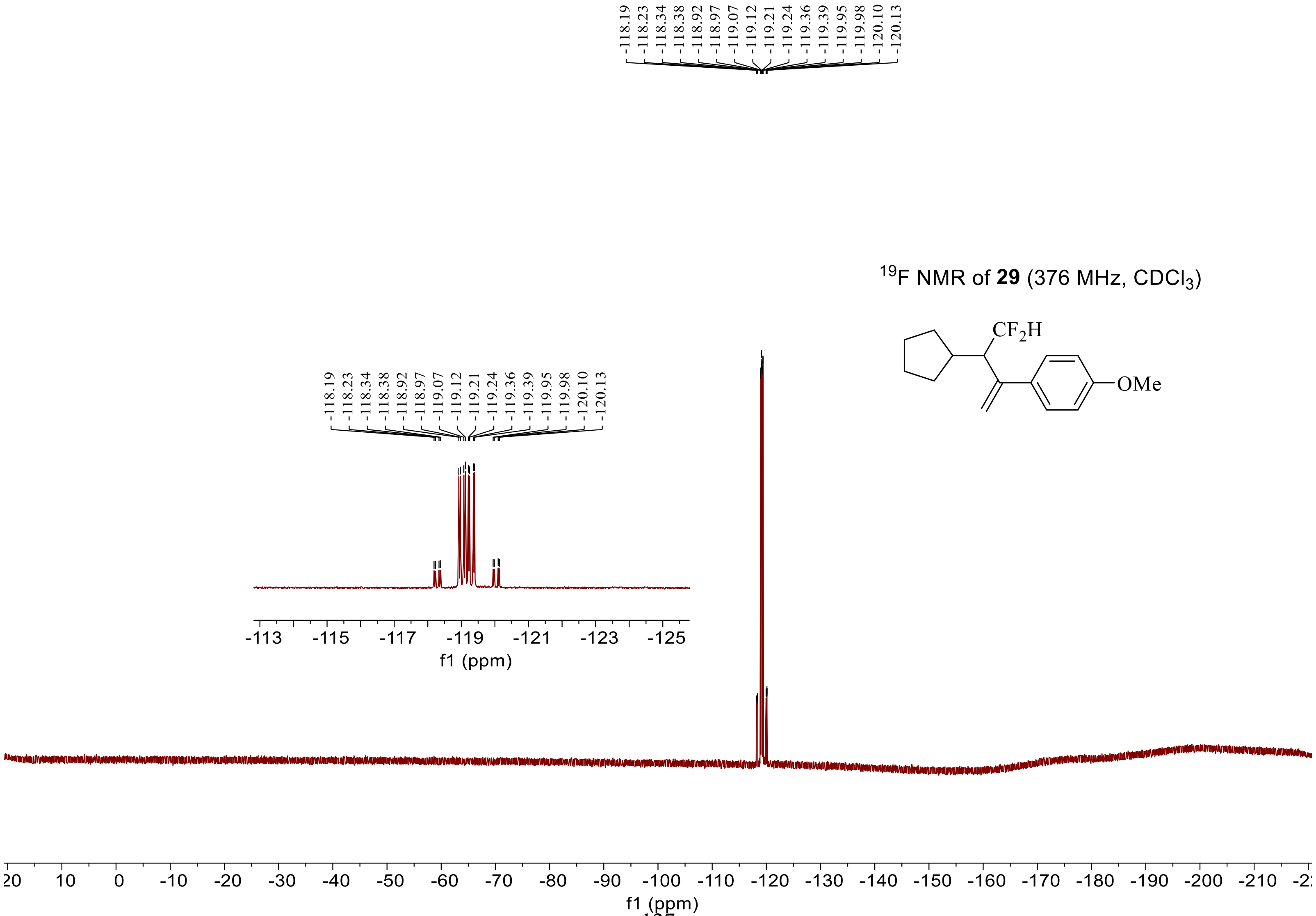




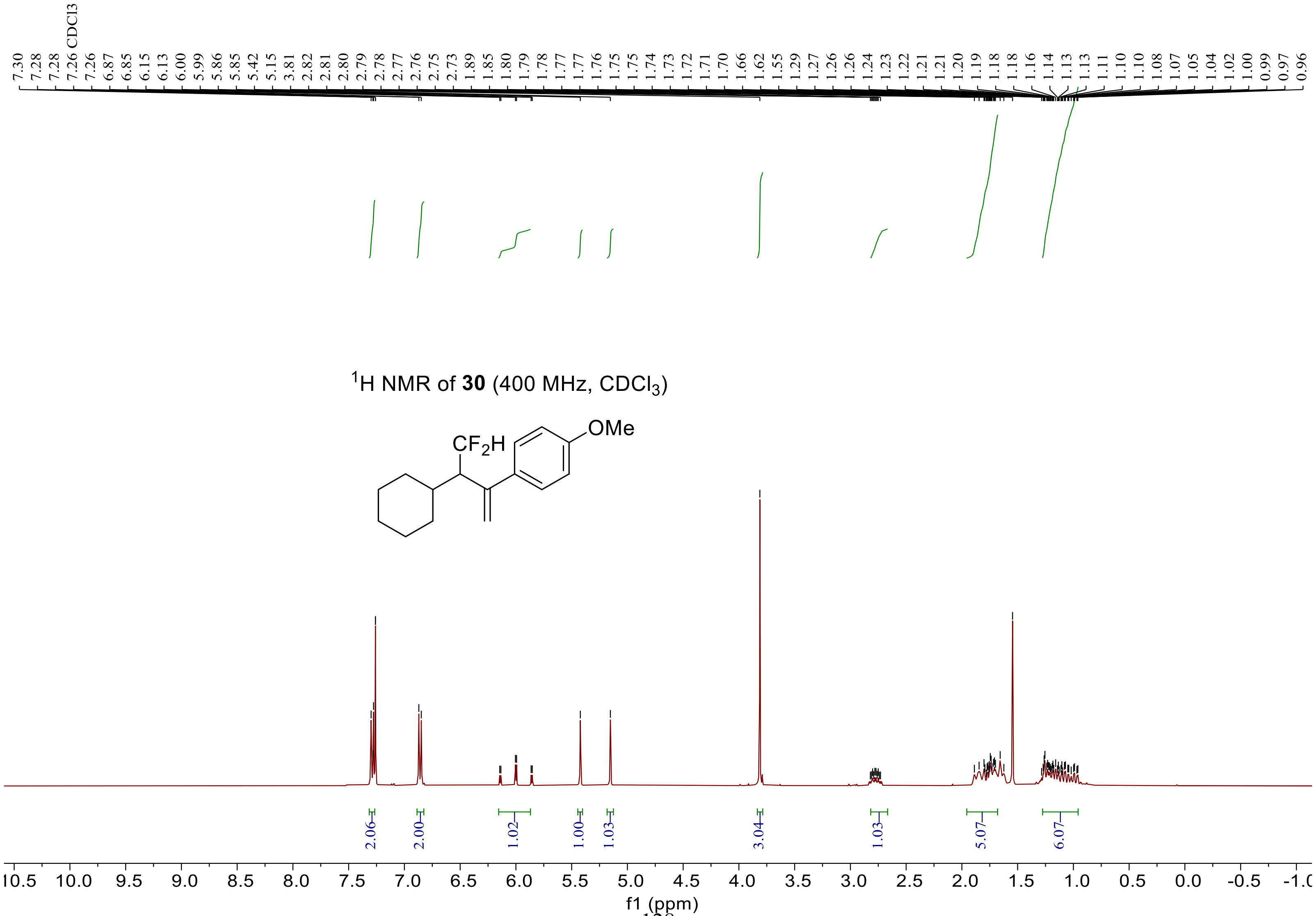
^{1}H NMR of **29** (400 MHz, $CDCl_3$)

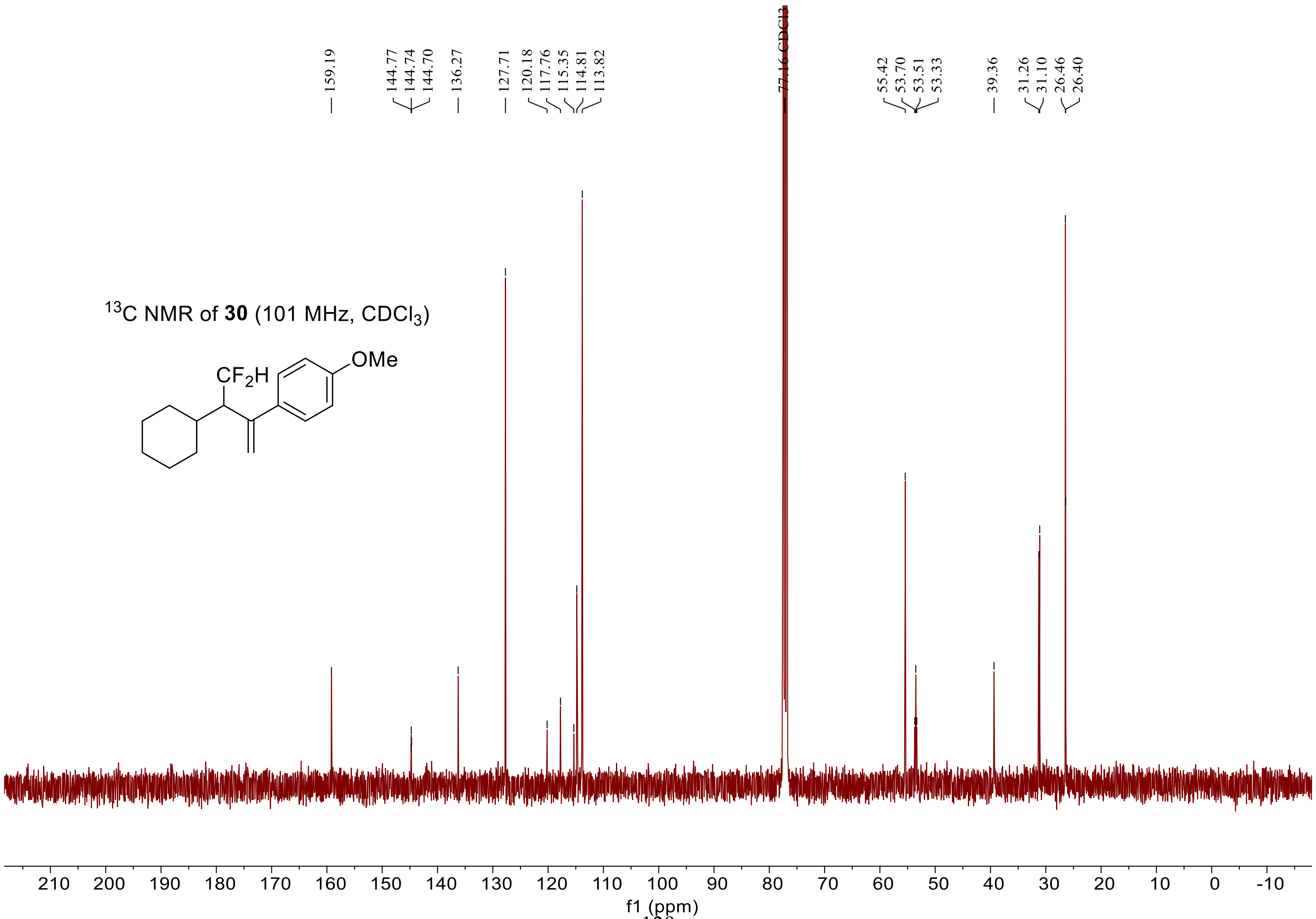
^{13}C NMR of **29** (101 MHz, $CDCl_3$)



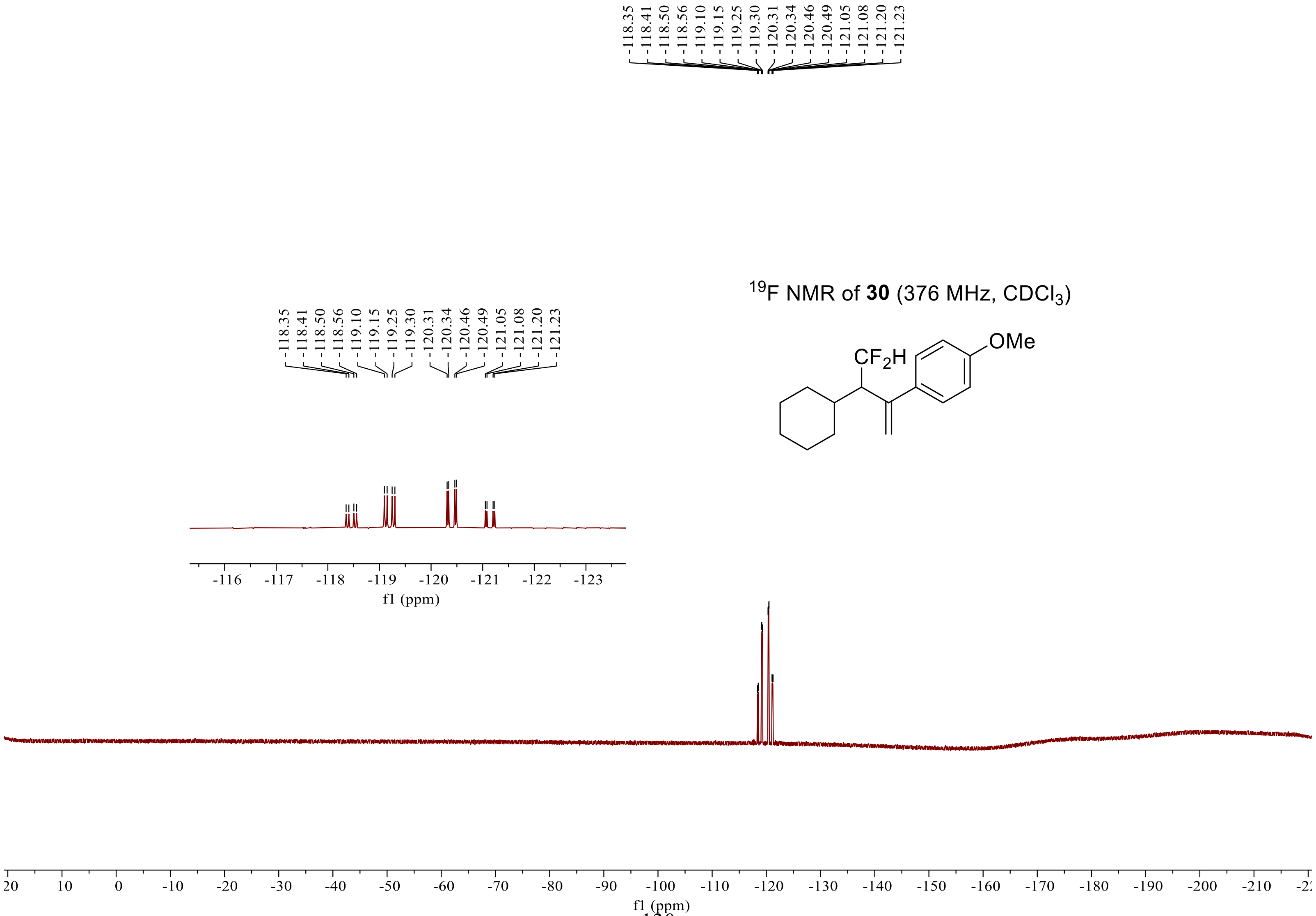


^{19}F NMR of **29** (376 MHz, $CDCl_3$)


7.30
7.28
7.26 CDCl3
7.26
6.87
6.85
6.15
6.13
6.00
5.99
5.86
5.85
5.42
5.15
3.81
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.75
2.73
1.89
1.85
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.71
1.70
1.66
1.62
1.55
1.29
1.27
1.26
1.26
1.24
1.23
1.22
1.21
1.21
1.20
1.19
1.18
1.18
1.16
1.14
1.13
1.13
1.11
1.10
1.10
1.08
1.07
1.05
1.04
1.02
1.00
0.99
0.97
0.96
^{1}H NMR of **30** (400 MHz, CDCl$_3$)
CF$_2$H
OMe
2.06
2.00
1.02
1.00
1.03
3.04
1.03
5.07
6.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

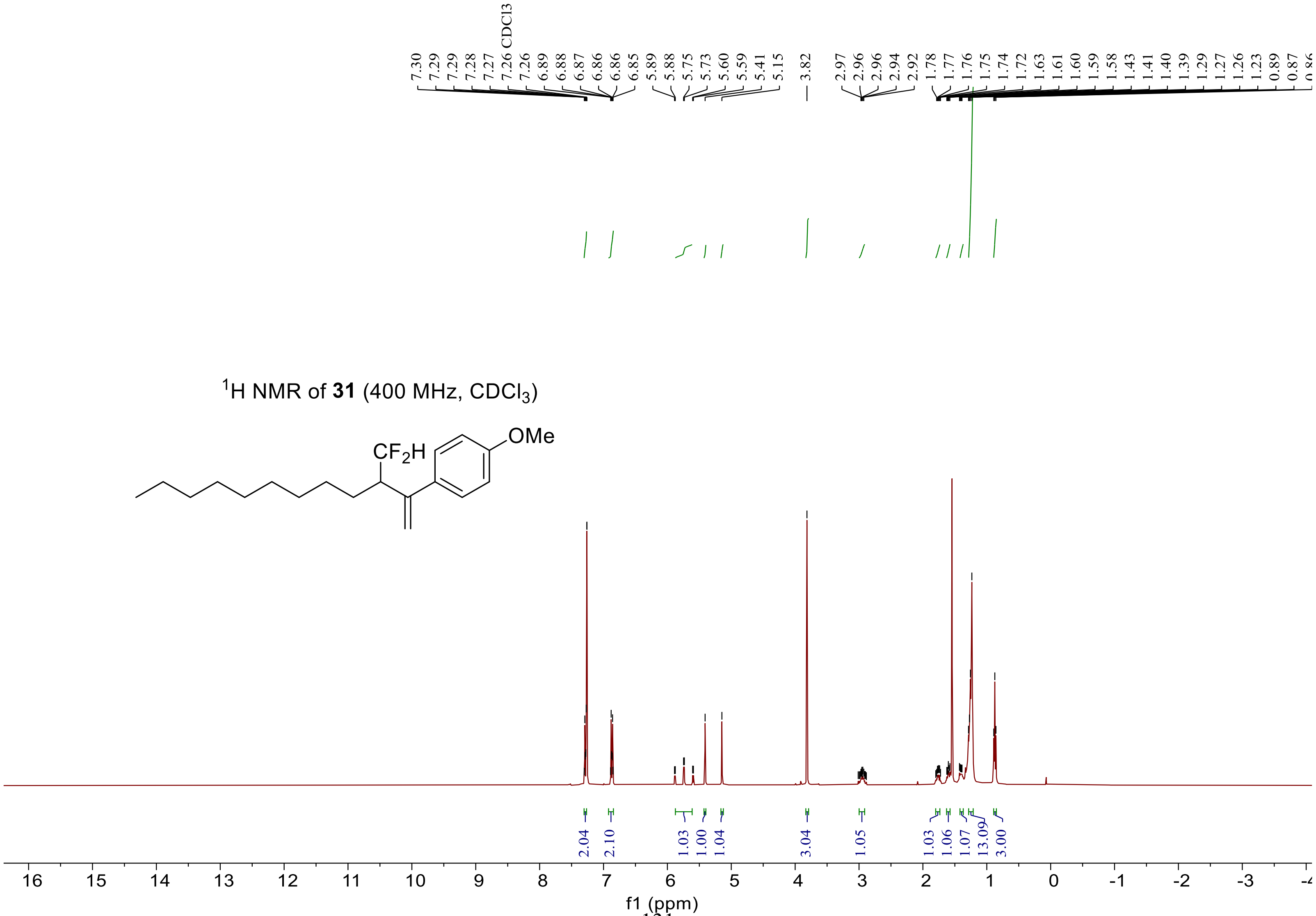


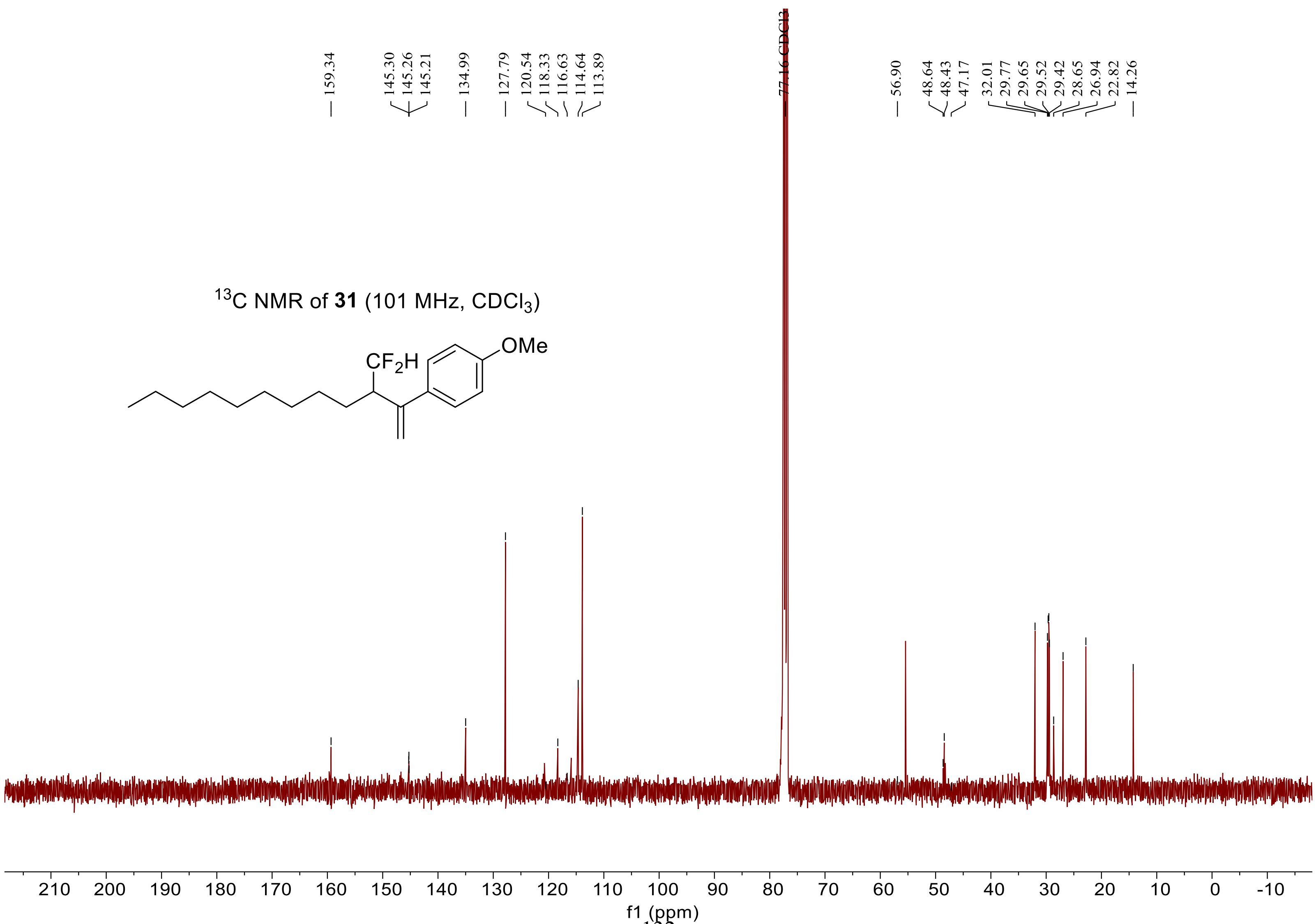
^{13}C NMR of **30** (101 MHz, CDCl$_3$)
CF$_2$H
OMe
159.19
144.77
144.74
144.70
136.27
127.71
120.18
117.76
115.35
114.81
113.82
77.16 CDCl3
55.42
53.70
53.51
53.33
39.36
31.26
31.10
26.46
26.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^{19}F NMR of **30** (376 MHz, $CDCl_3$)

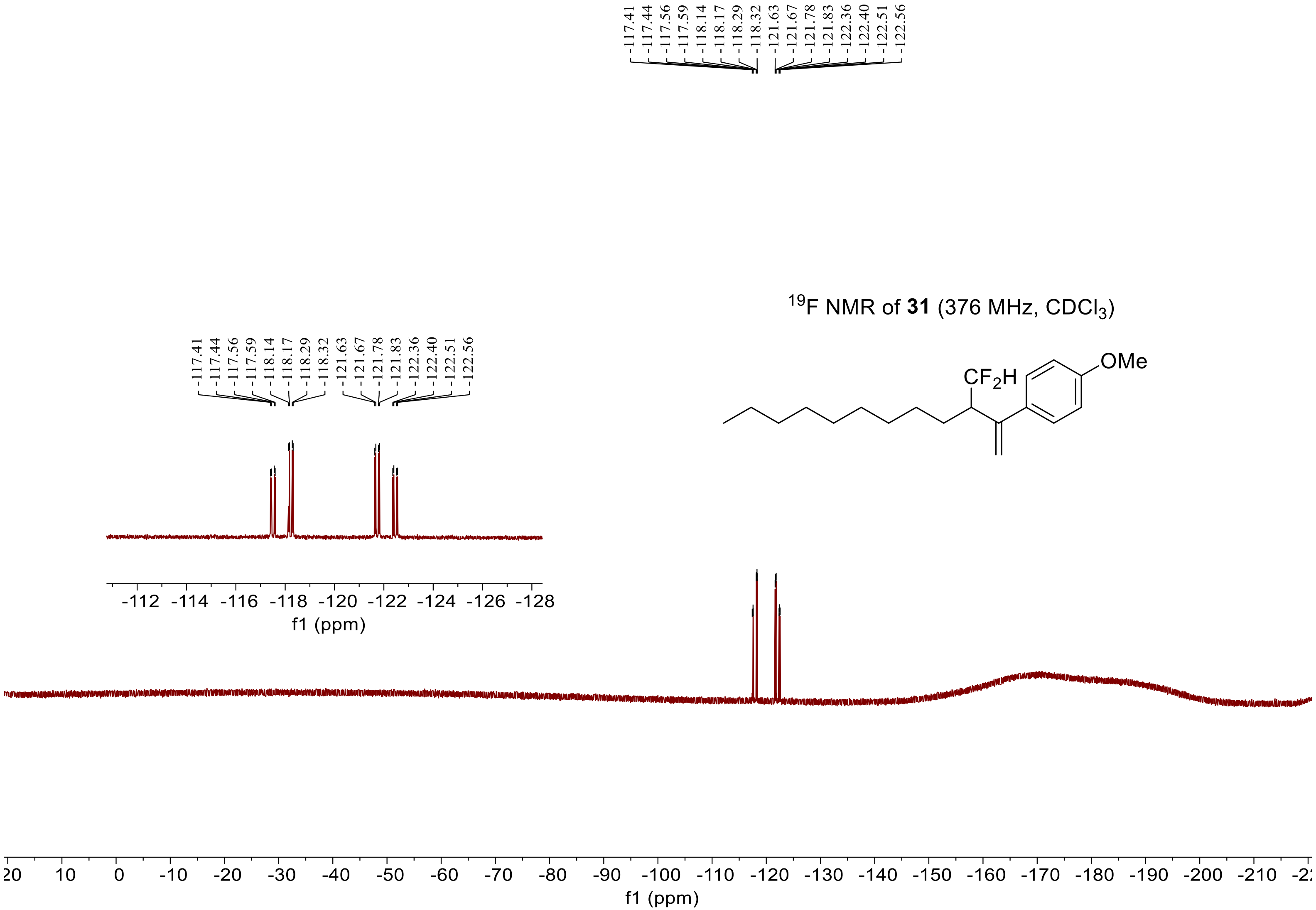
^{1}H NMR of **31** (400 MHz, $CDCl_3$)

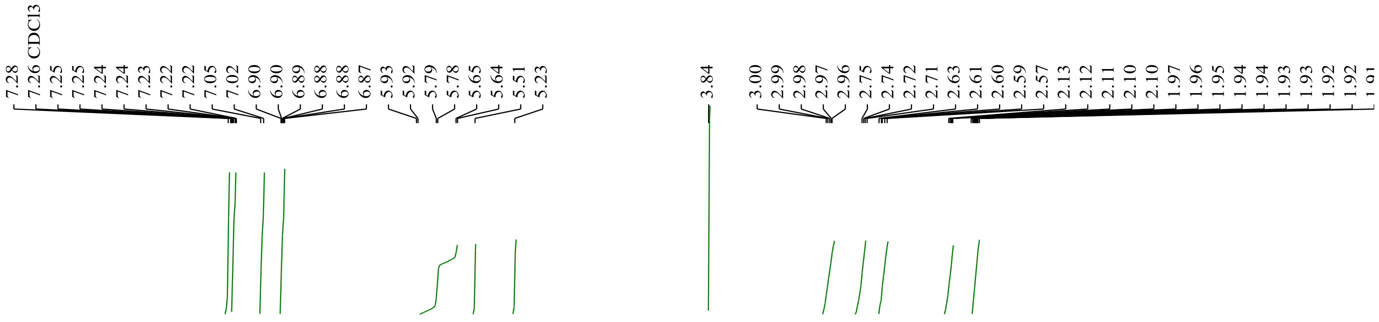




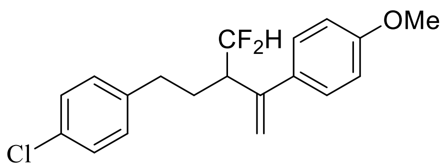
159.34
145.30
145.26
145.21
134.99
127.79
120.54
118.33
116.63
114.64
113.89
77.16 CDCl3
56.90
48.64
48.43
47.17
32.01
29.77
29.65
29.52
29.42
28.65
26.94
22.82
14.26
^{13}C NMR of **31** (101 MHz, $CDCl_3$)
CF_2H
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

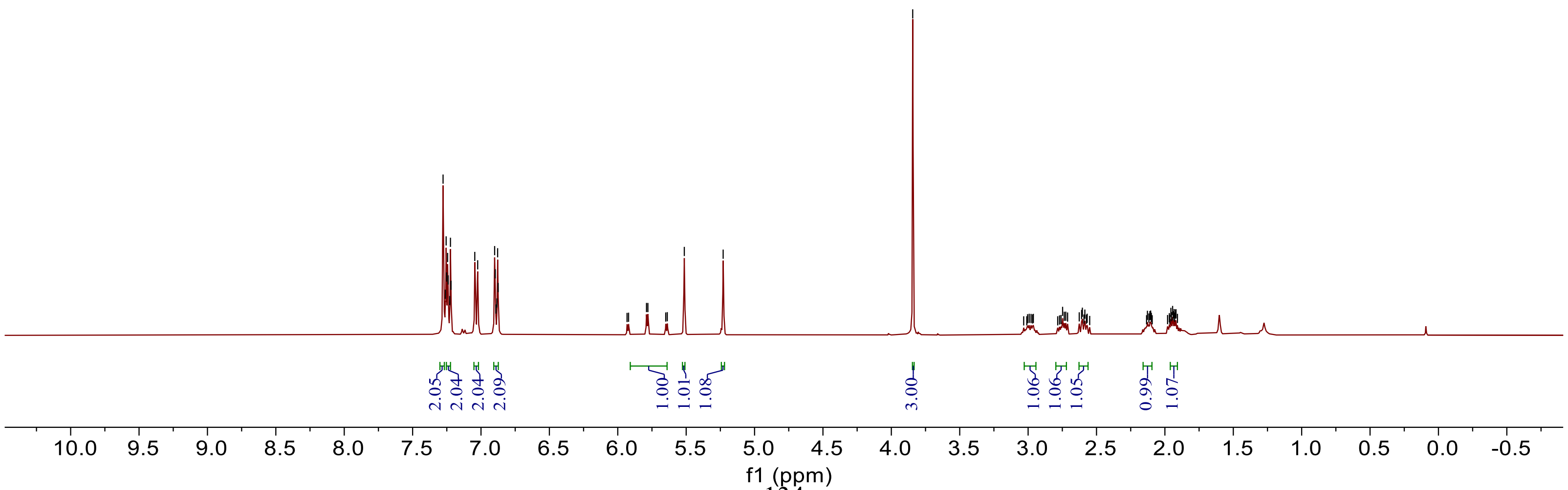
^{19}F NMR of **31** (376 MHz, $CDCl_3$)

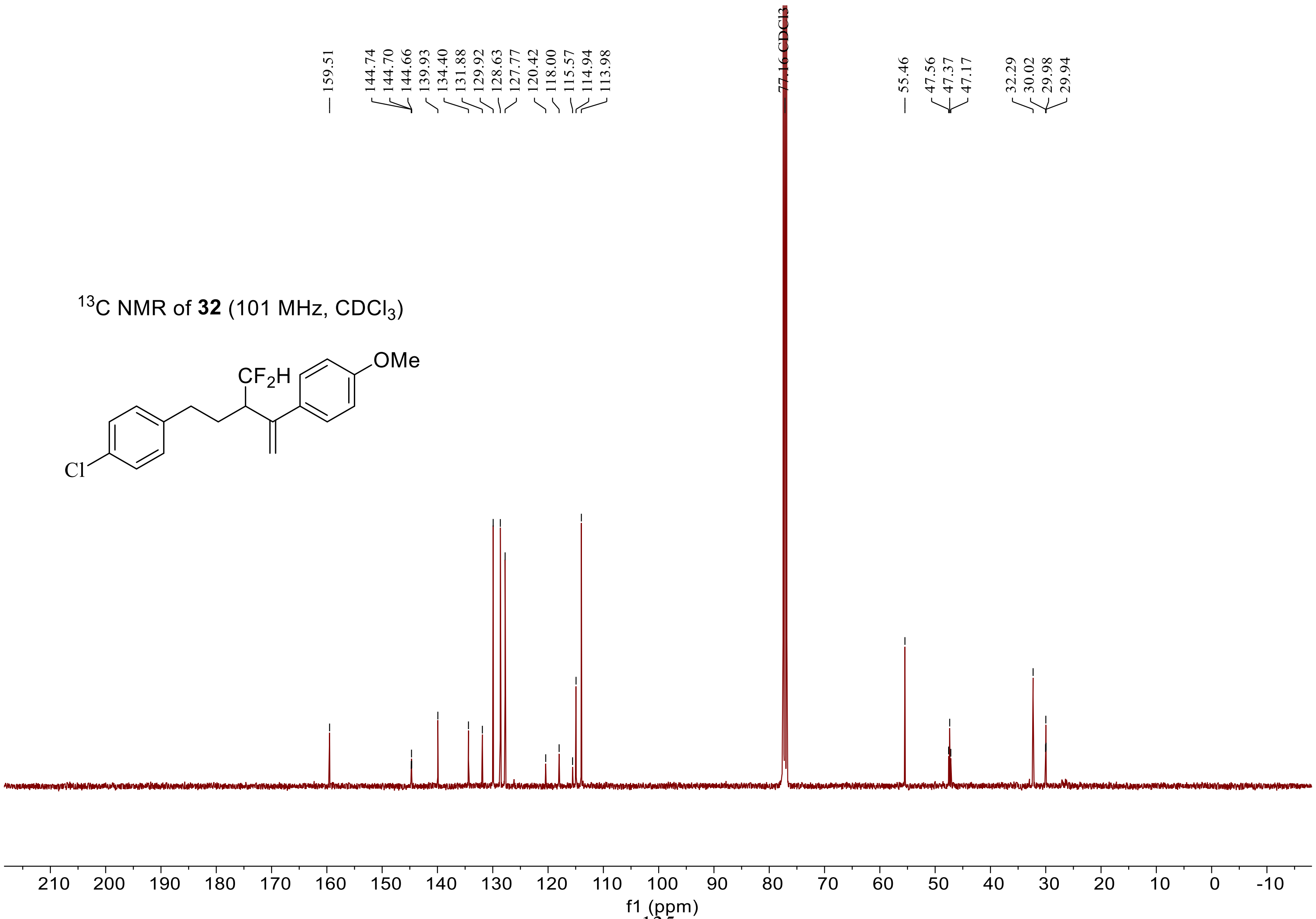




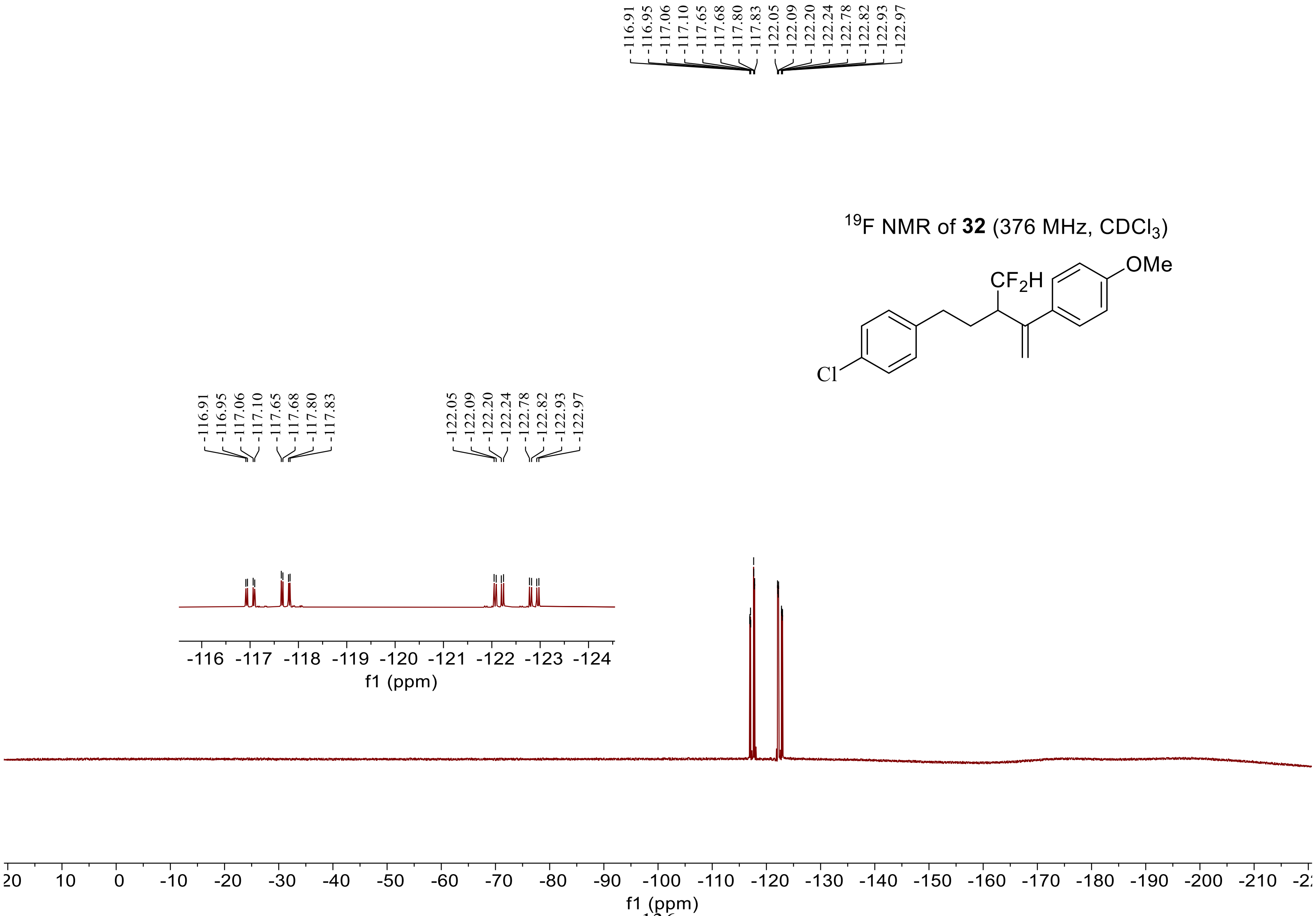
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



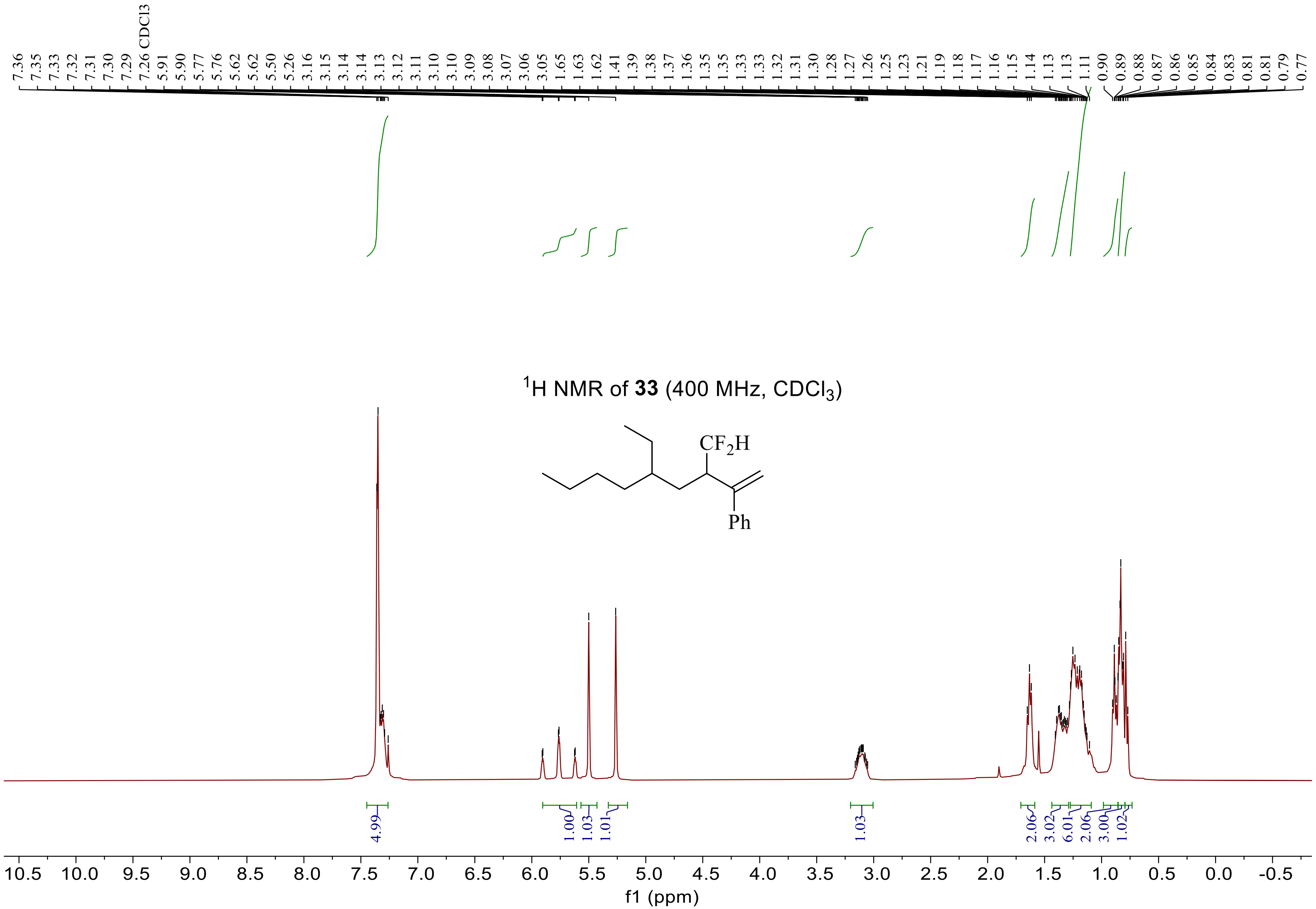




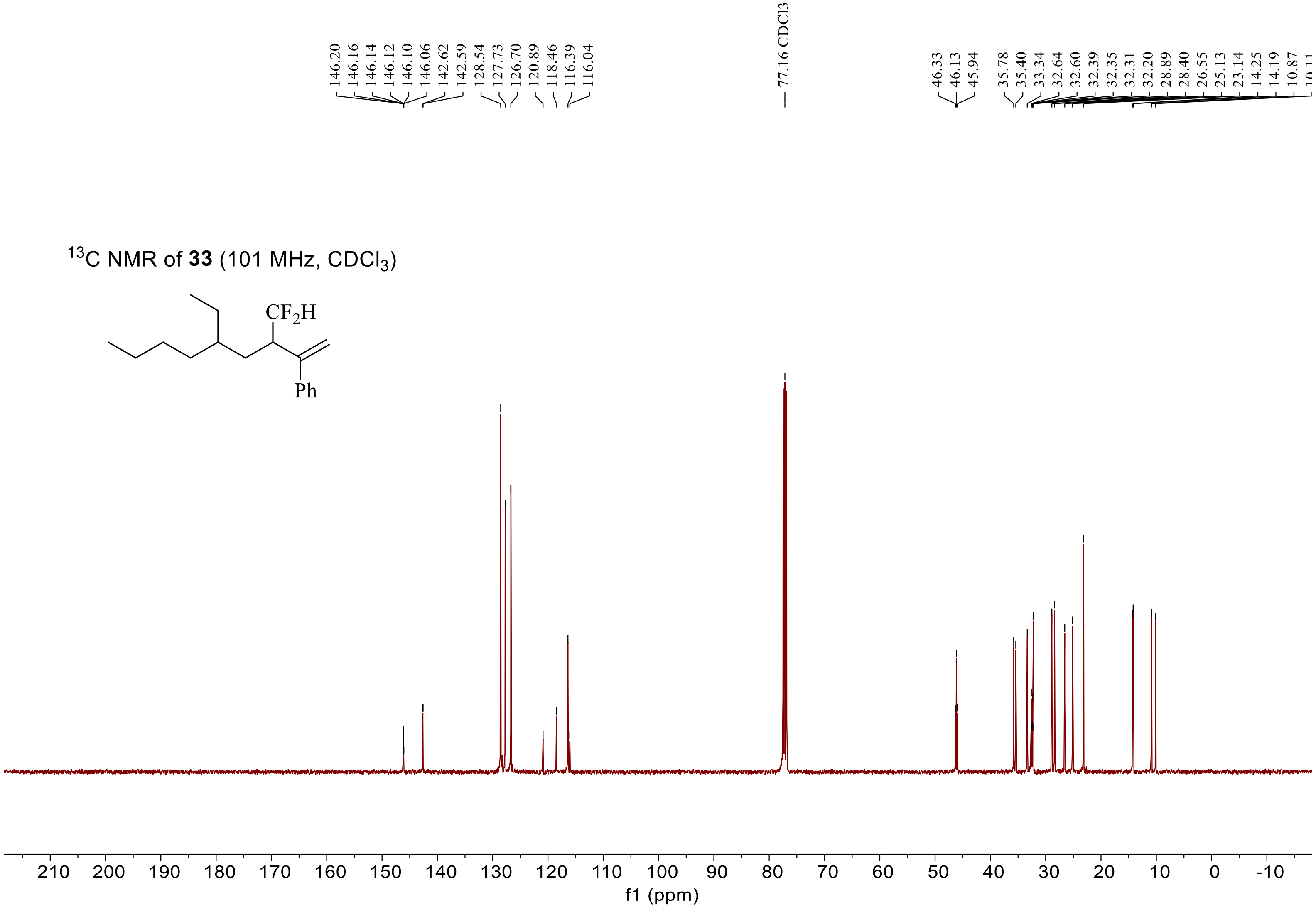
^{13}C NMR of **32** (101 MHz, $CDCl_3$)

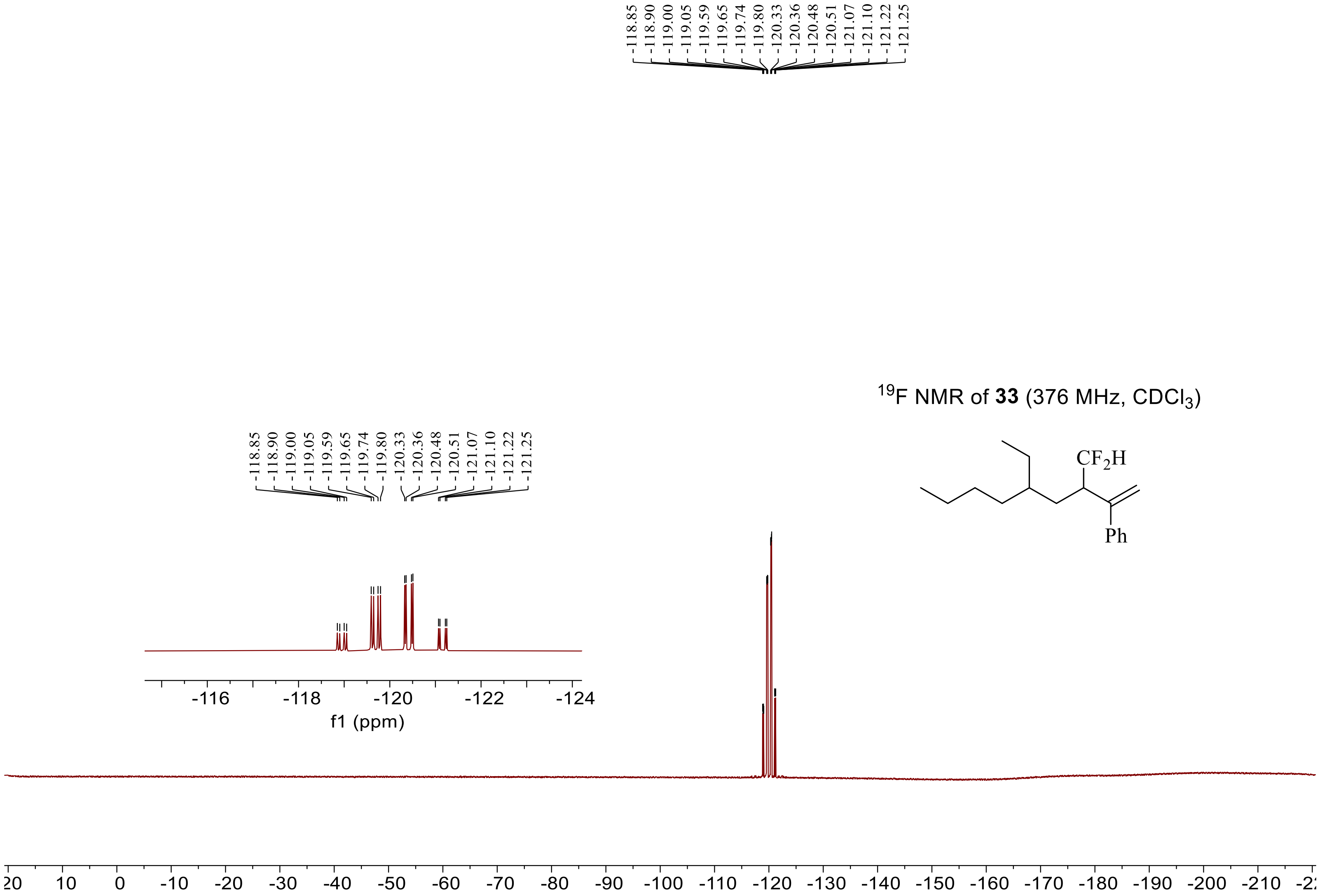


^{19}F NMR of **32** (376 MHz, $CDCl_3$)

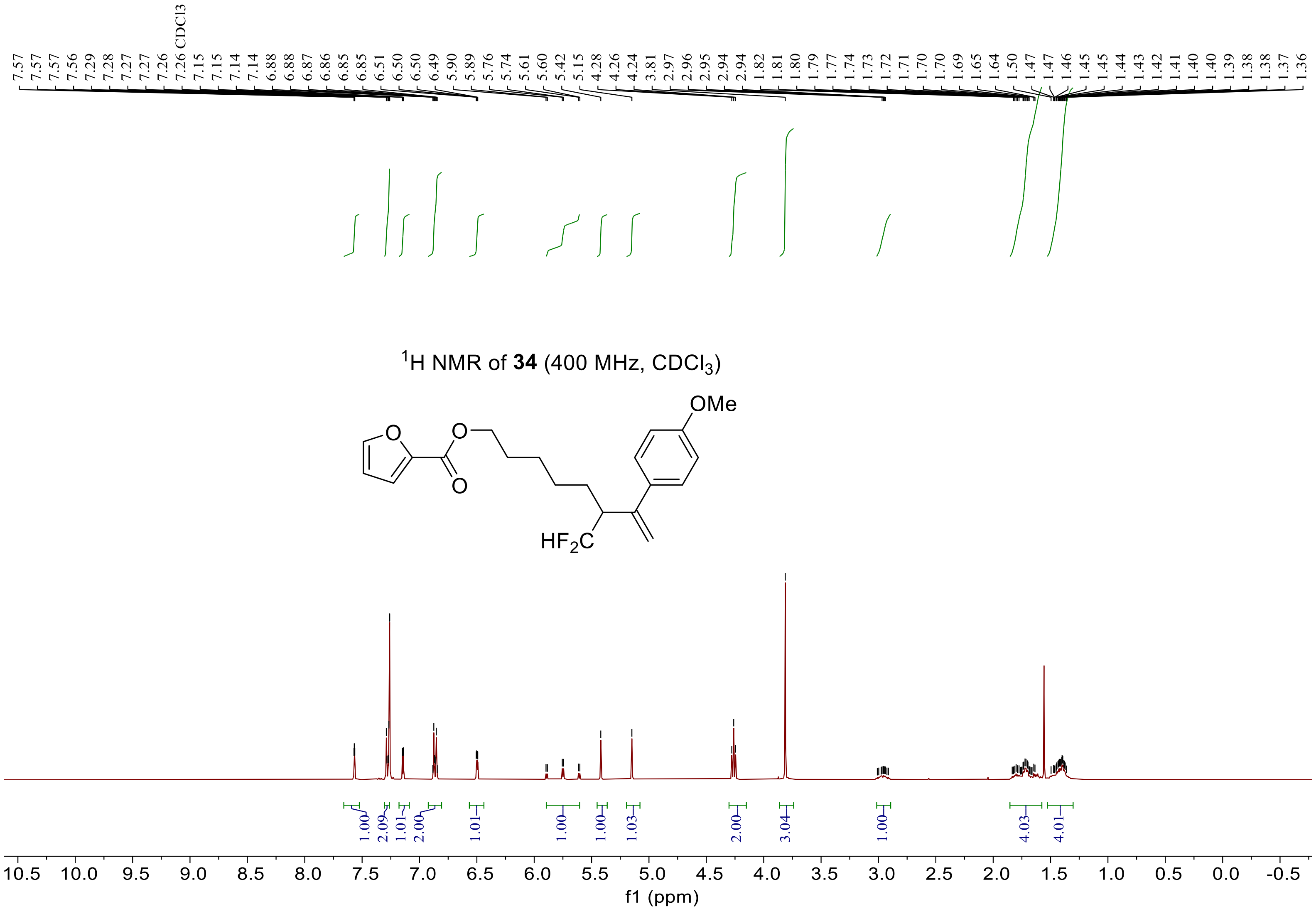

7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.26 CDCl3
5.91
5.90
5.77
5.76
5.62
5.62
5.50
5.26
3.16
3.15
3.14
3.14
3.13
3.12
3.11
3.10
3.10
3.09
3.08
3.07
3.06
3.05
1.65
1.63
1.62
1.41
1.39
1.38
1.37
1.36
1.35
1.35
1.33
1.33
1.32
1.31
1.30
1.28
1.27
1.26
1.25
1.23
1.21
1.19
1.18
1.17
1.16
1.15
1.14
1.13
1.13
1.11
0.90
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.81
0.81
0.79
0.77
^{1}H NMR of **33** (400 MHz, CDCl$_3$)
CF$_2$H
Ph
4.99
1.00
1.03
1.01
1.03
2.06
3.02
6.01
2.06
3.00
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C NMR of **33** (101 MHz, $CDCl_3$)

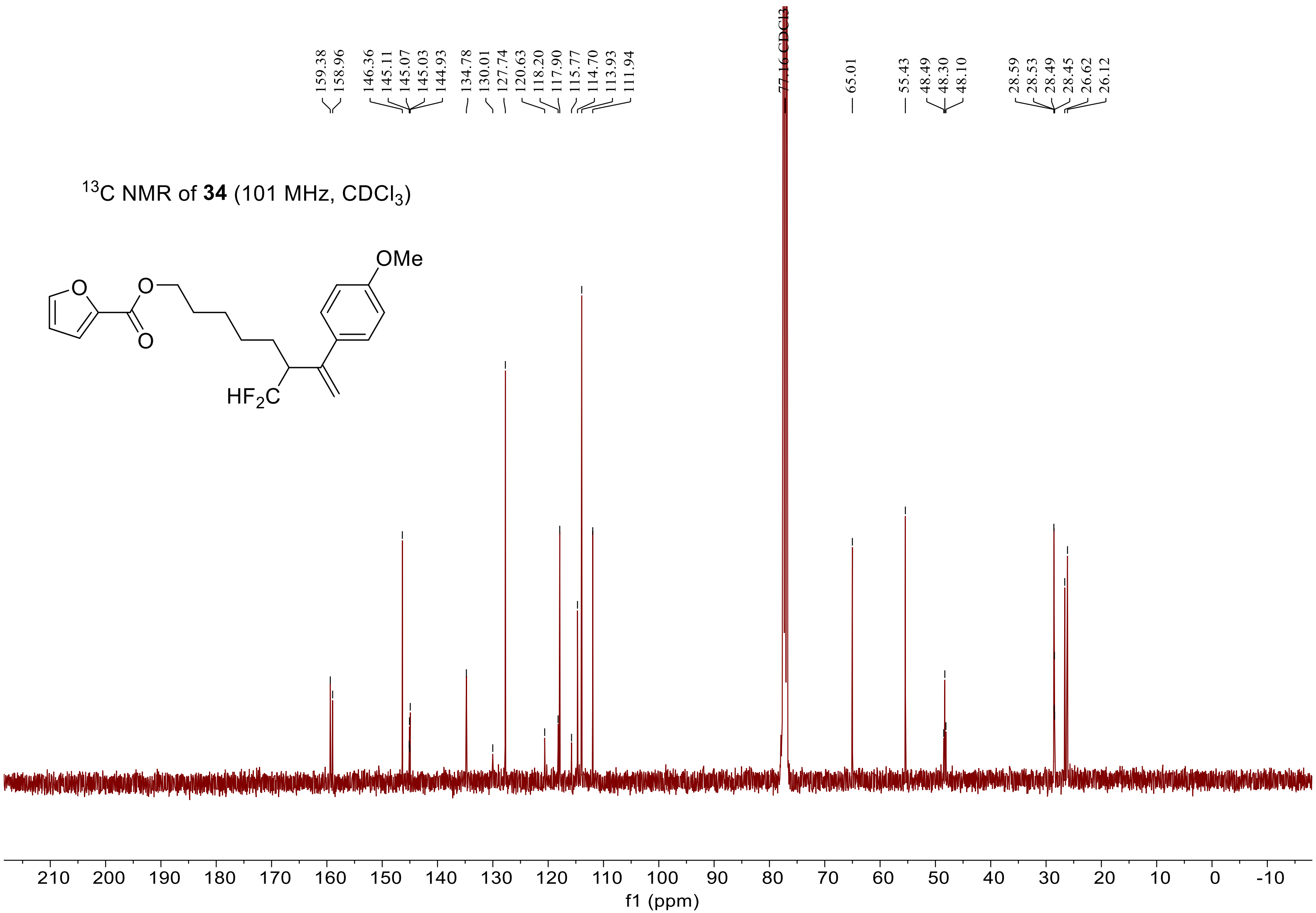



-118.85
-118.90
-119.00
-119.05
-119.59
-119.65
-119.74
-119.80
-120.33
-120.36
-120.48
-120.51
-121.07
-121.10
-121.22
-121.25
^{19}F NMR of **33** (376 MHz, CDCl$_3$)
CF$_2$H
Ph
-116
-118
-120
-122
-124
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

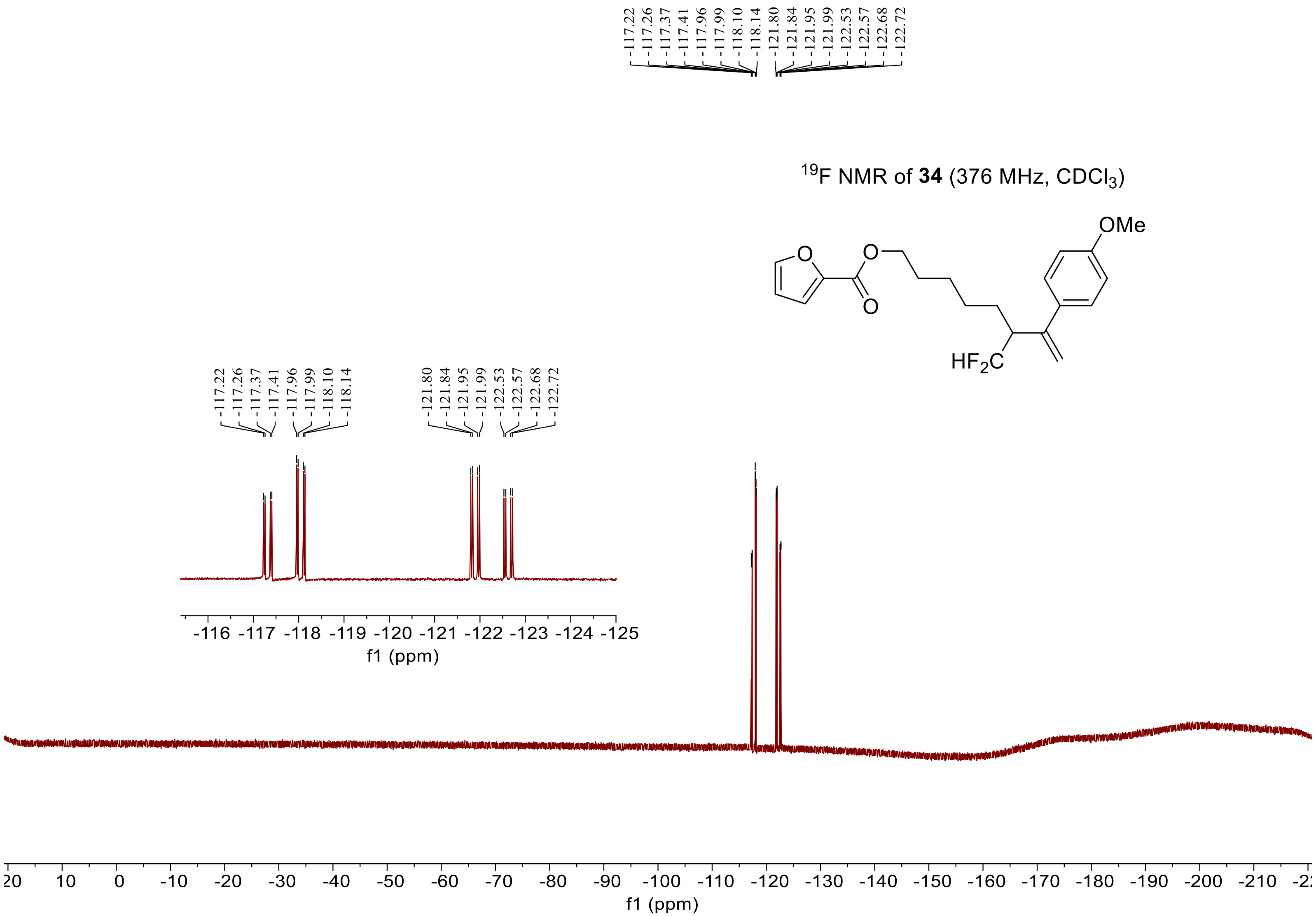
[1]H NMR of **34** (400 MHz, $CDCl_3$)

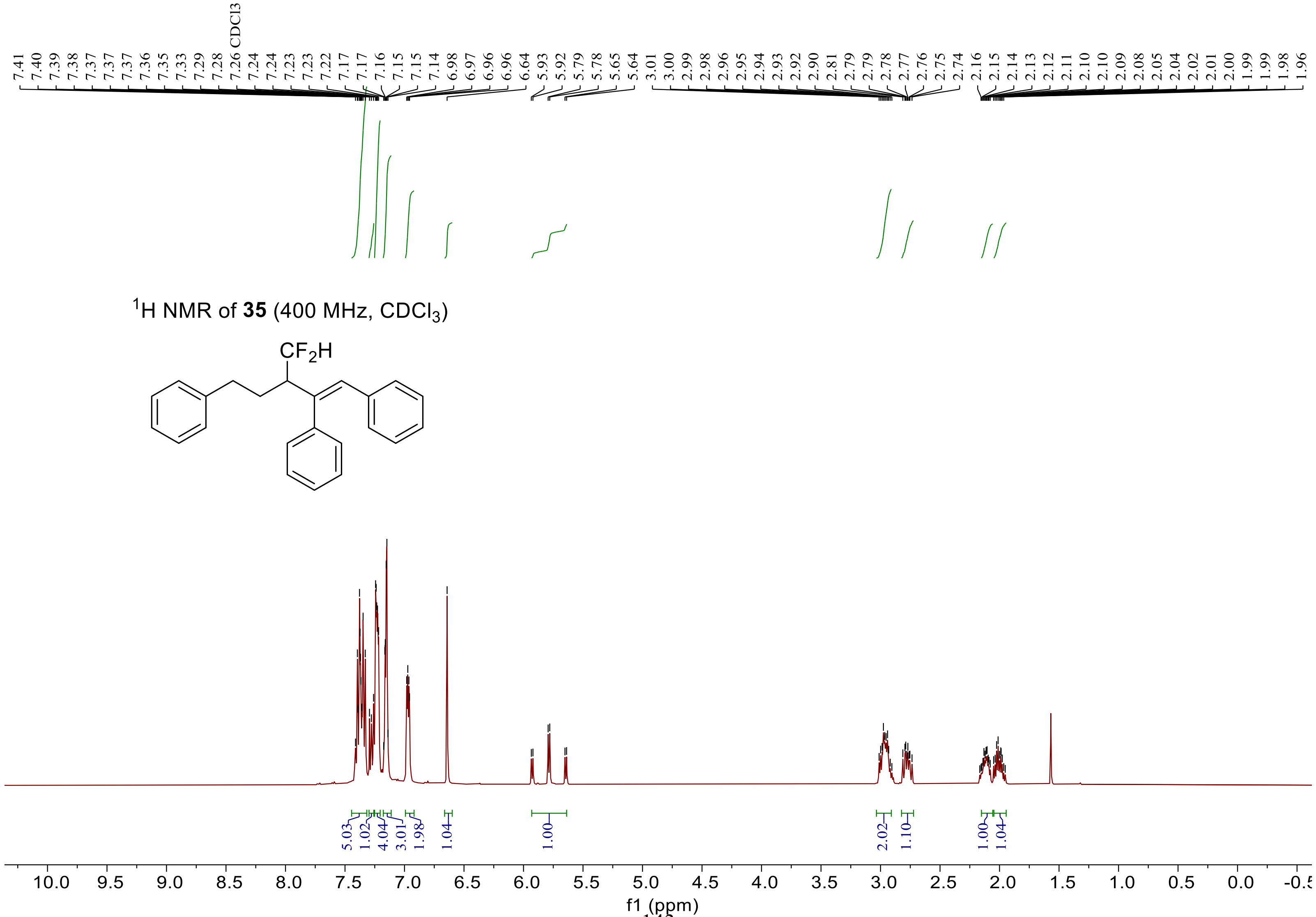


^{13}C NMR of **34** (101 MHz, $CDCl_3$)

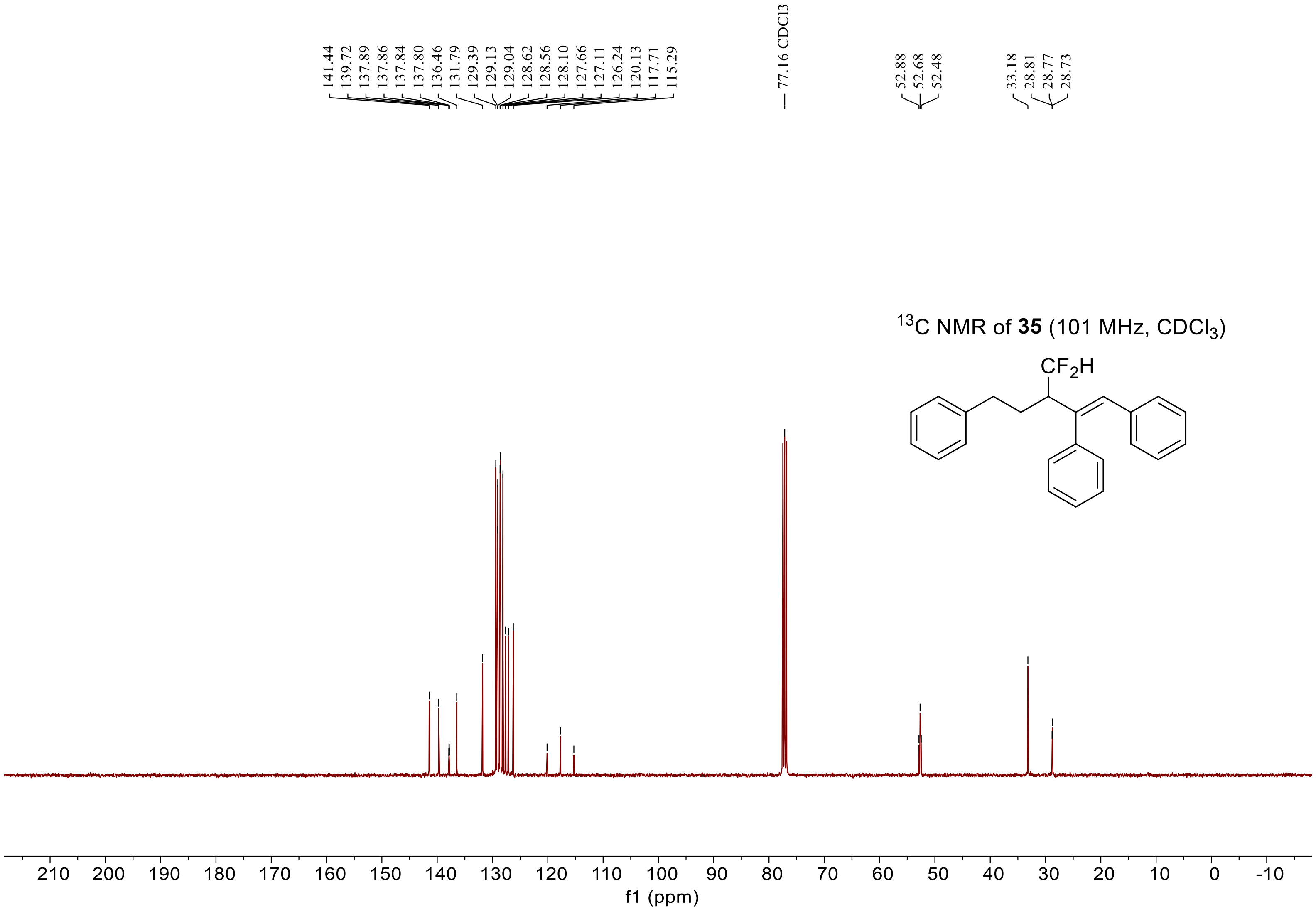


^{19}F NMR of **34** (376 MHz, $CDCl_3$)



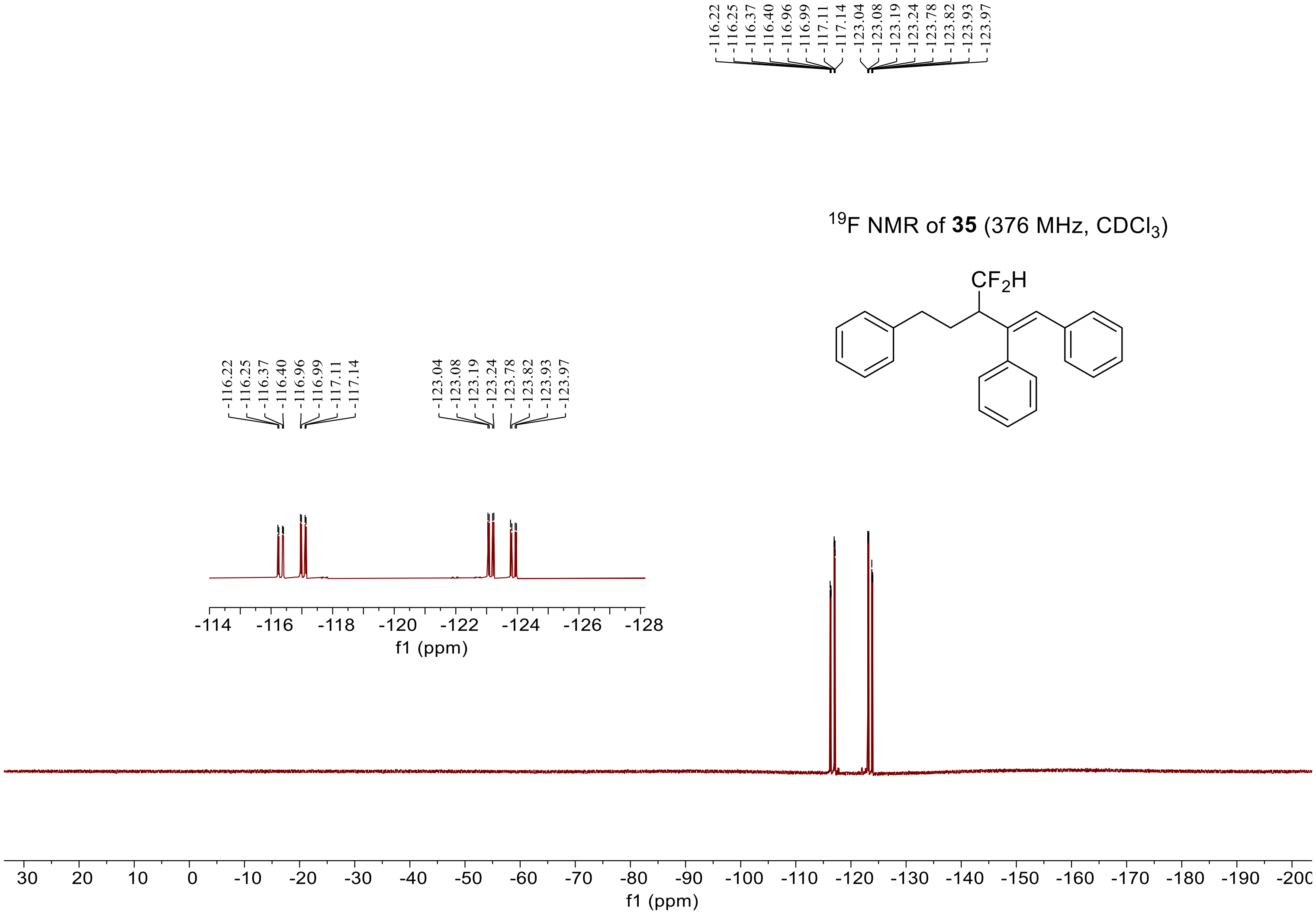


^{1}H NMR of **35** (400 MHz, $CDCl_3$)

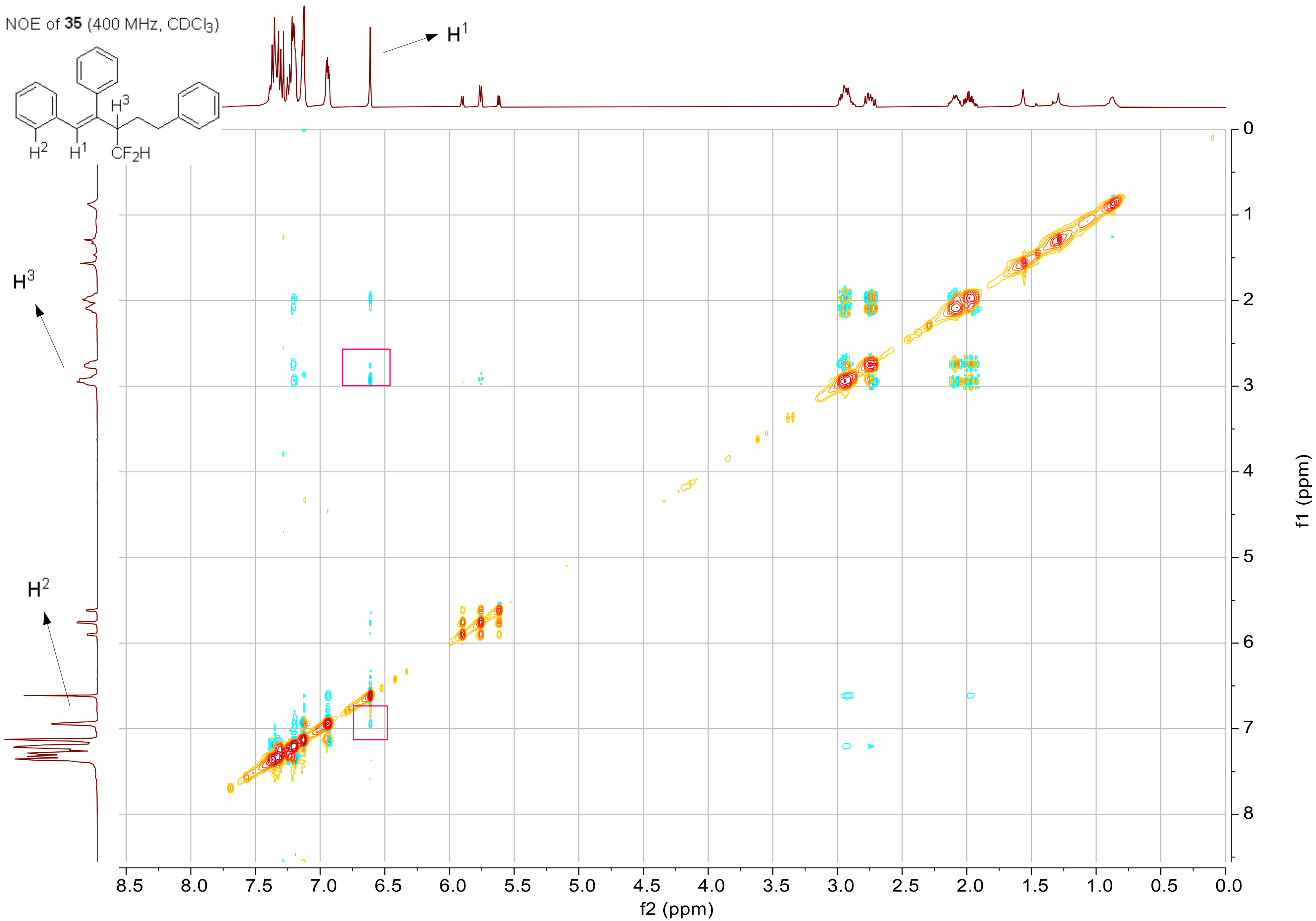


^{13}C NMR of **35** (101 MHz, $CDCl_3$)

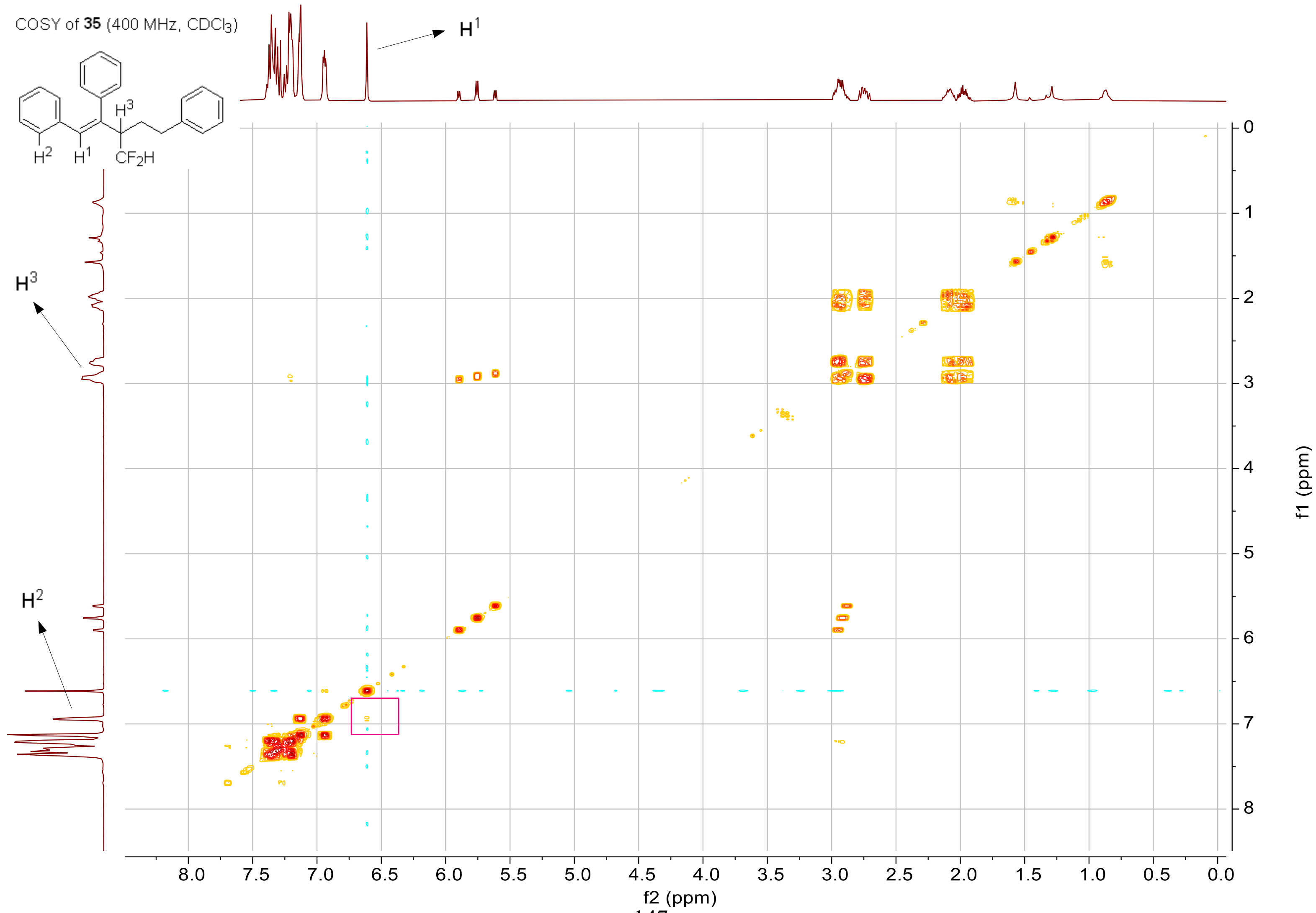
^{19}F NMR of **35** (376 MHz, $CDCl_3$)

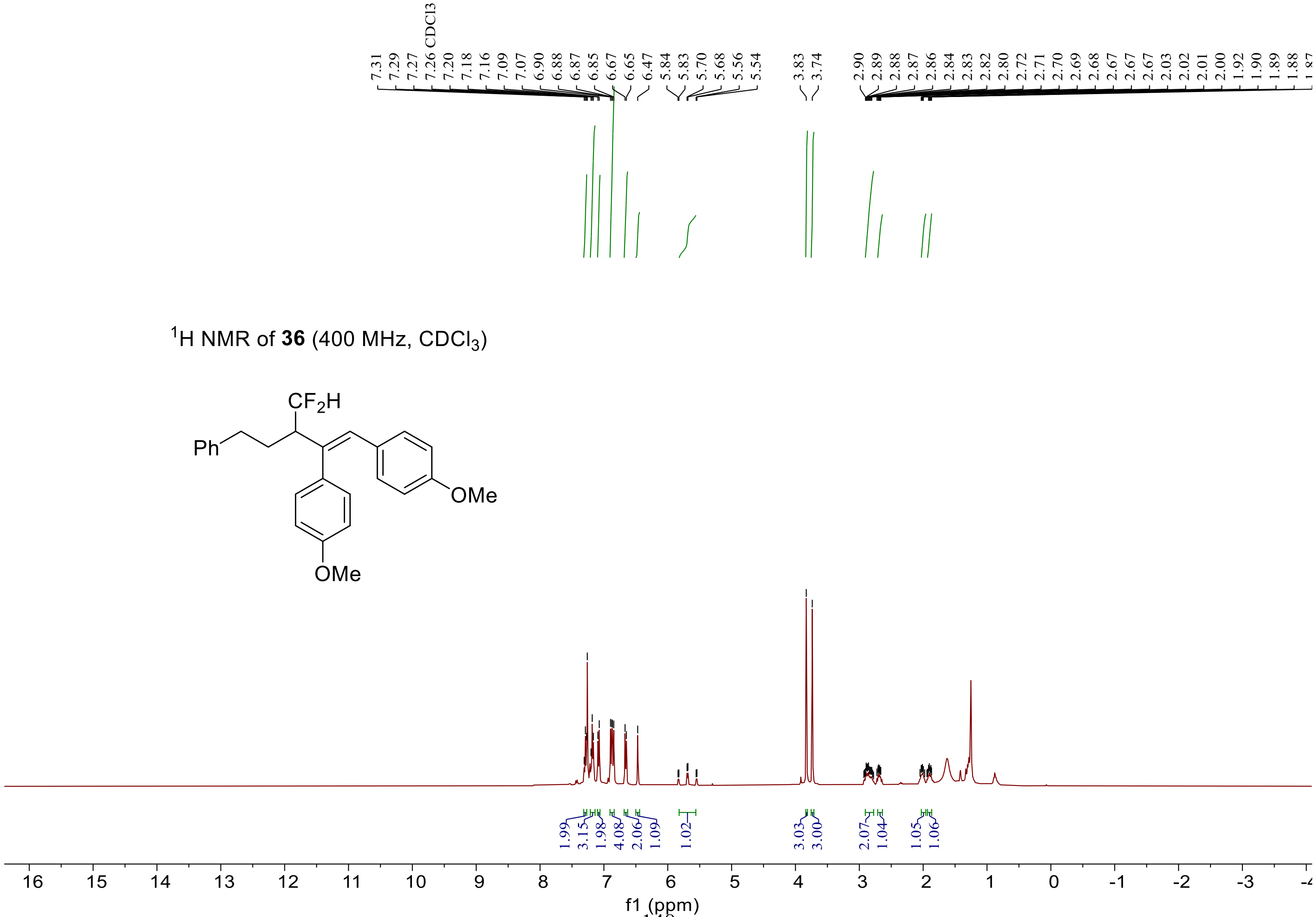


NOE of **35** (400 MHz, $CDCl_3$)



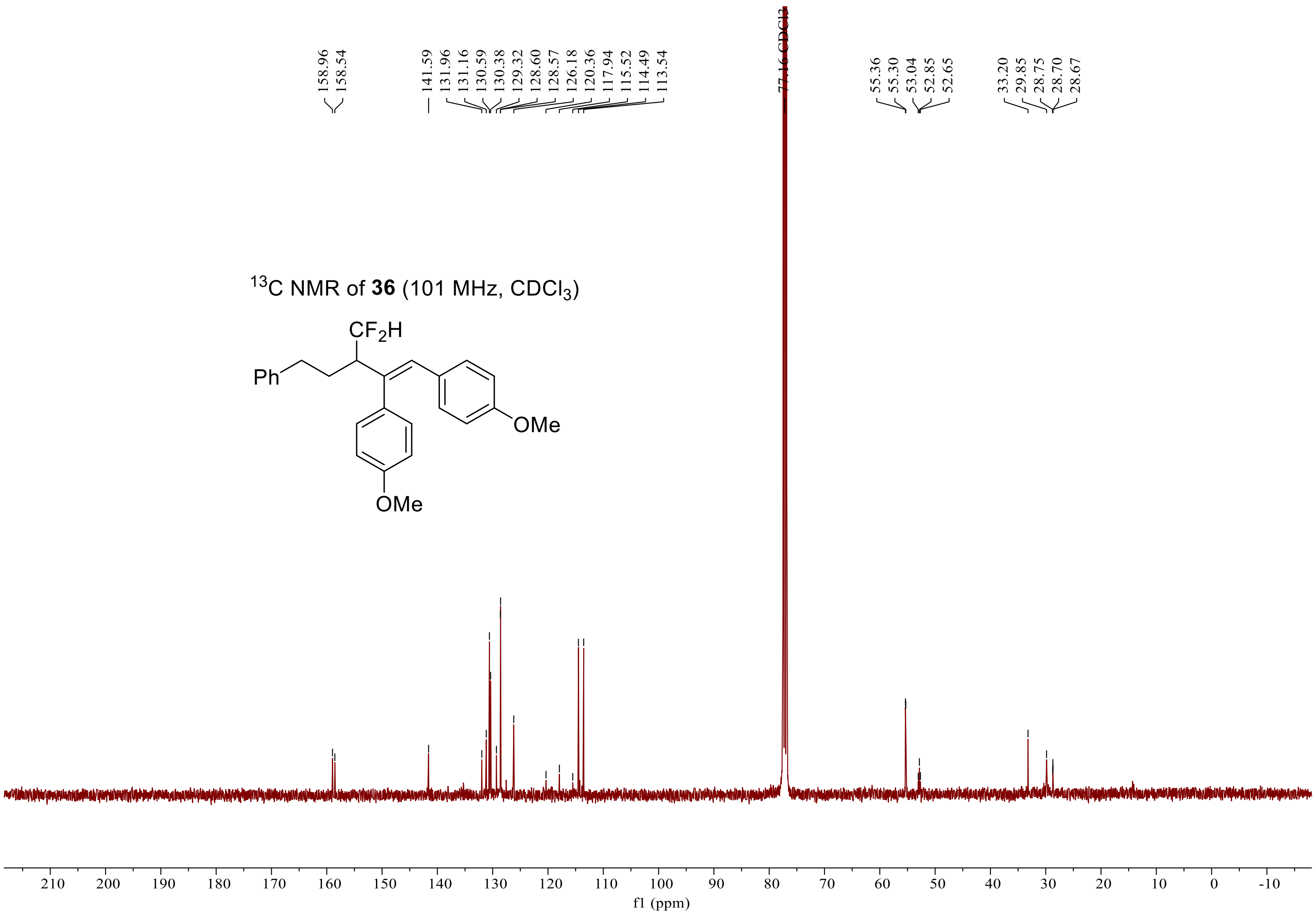
COSY of **35** (400 MHz, $CDCl_3$)



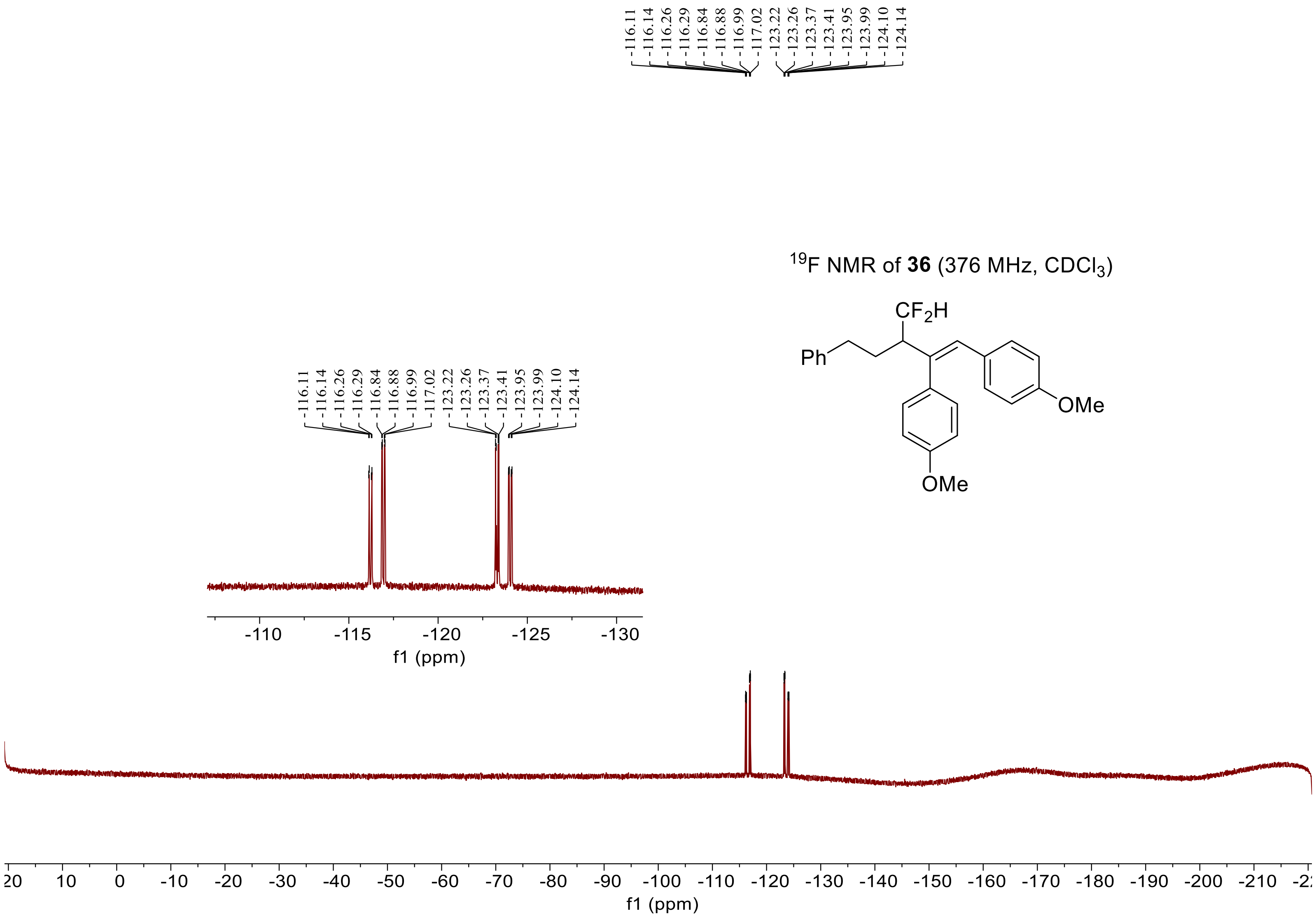


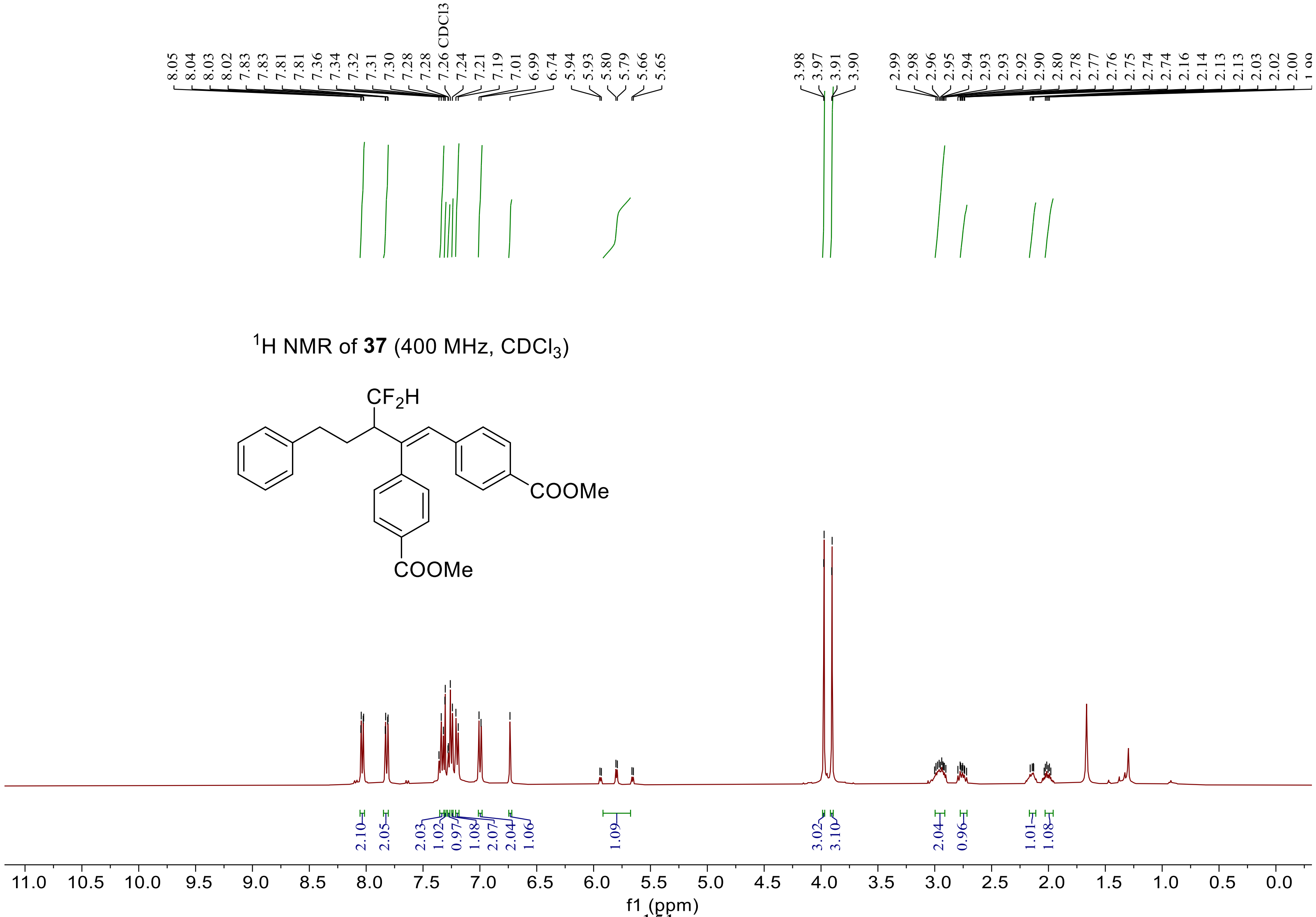
^{1}H NMR of **36** (400 MHz, $CDCl_3$)

^{13}C NMR of **36** (101 MHz, $CDCl_3$)

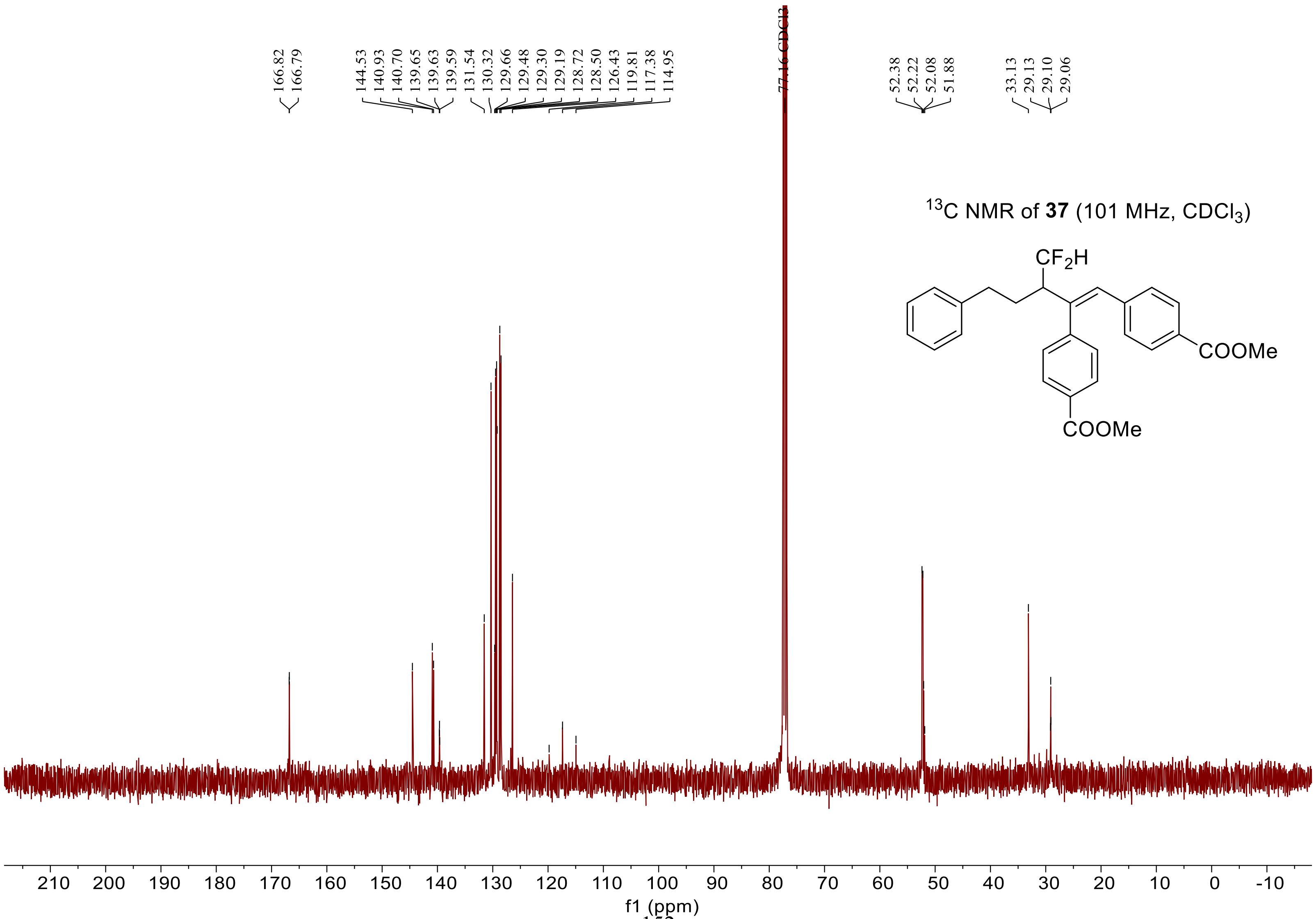


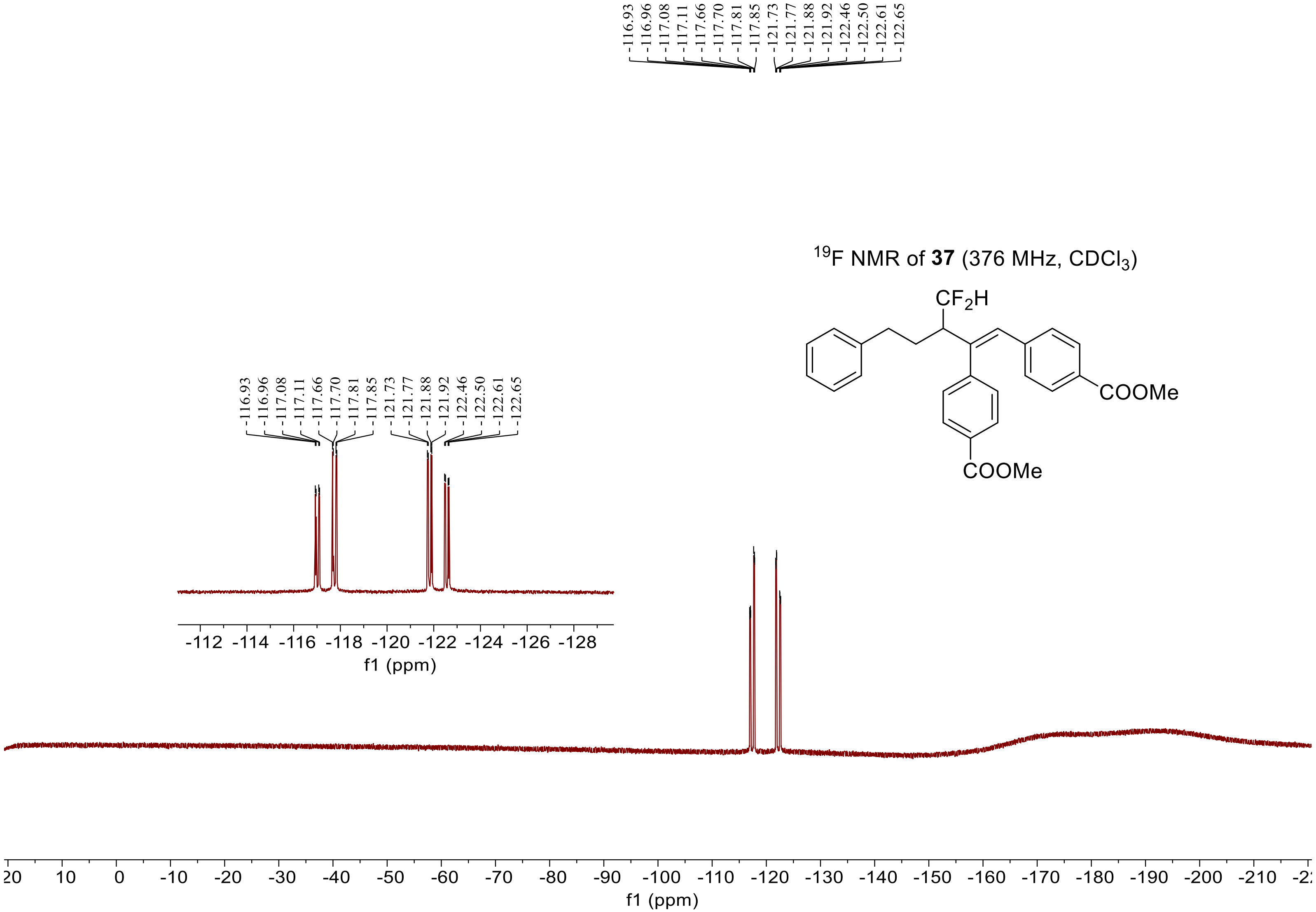
^{19}F NMR of **36** (376 MHz, $CDCl_3$)





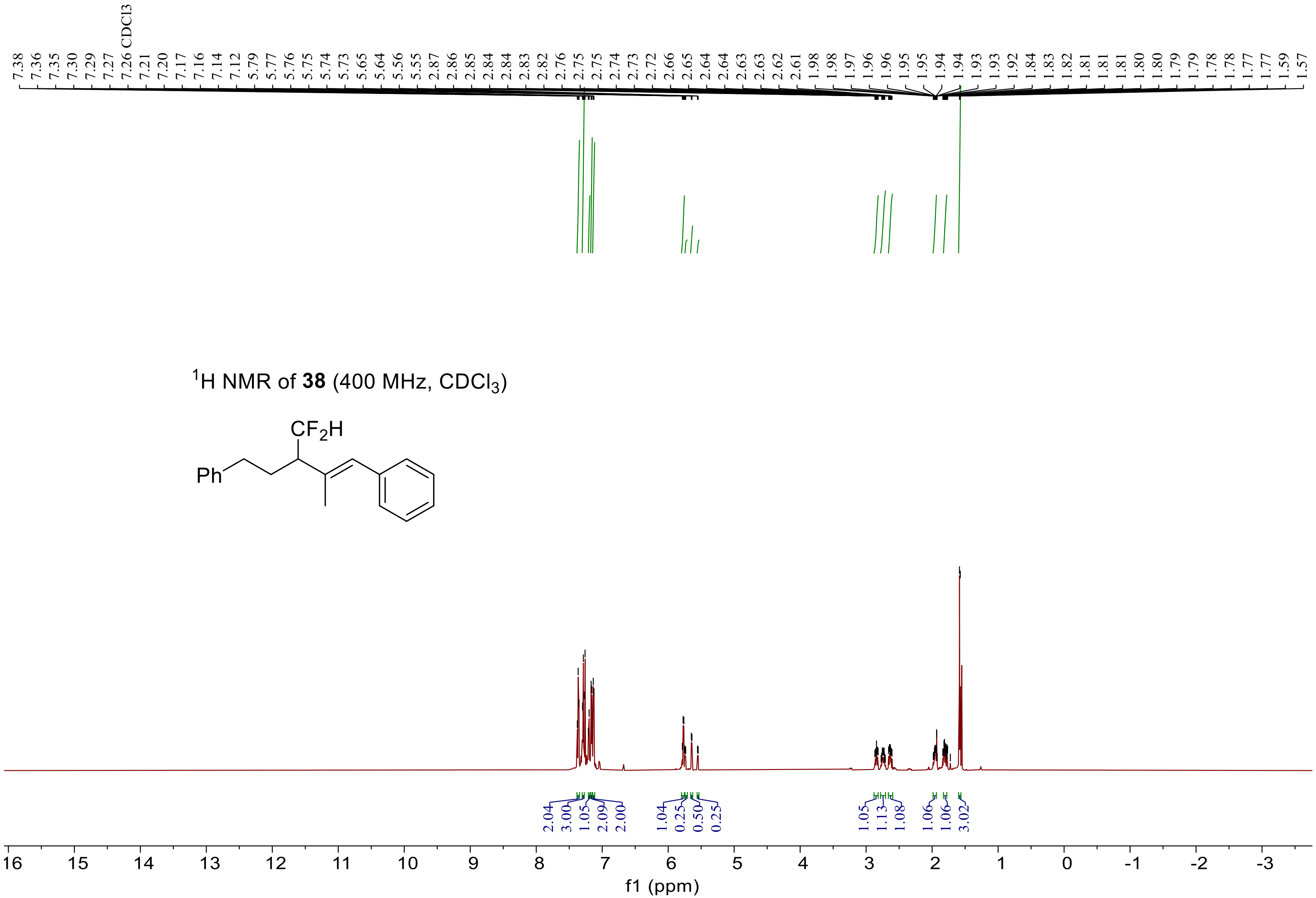
CDCl3
^{1}H NMR of **37** (400 MHz, $CDCl_3$)
CF_2H
COOMe
COOMe
f1 (ppm)

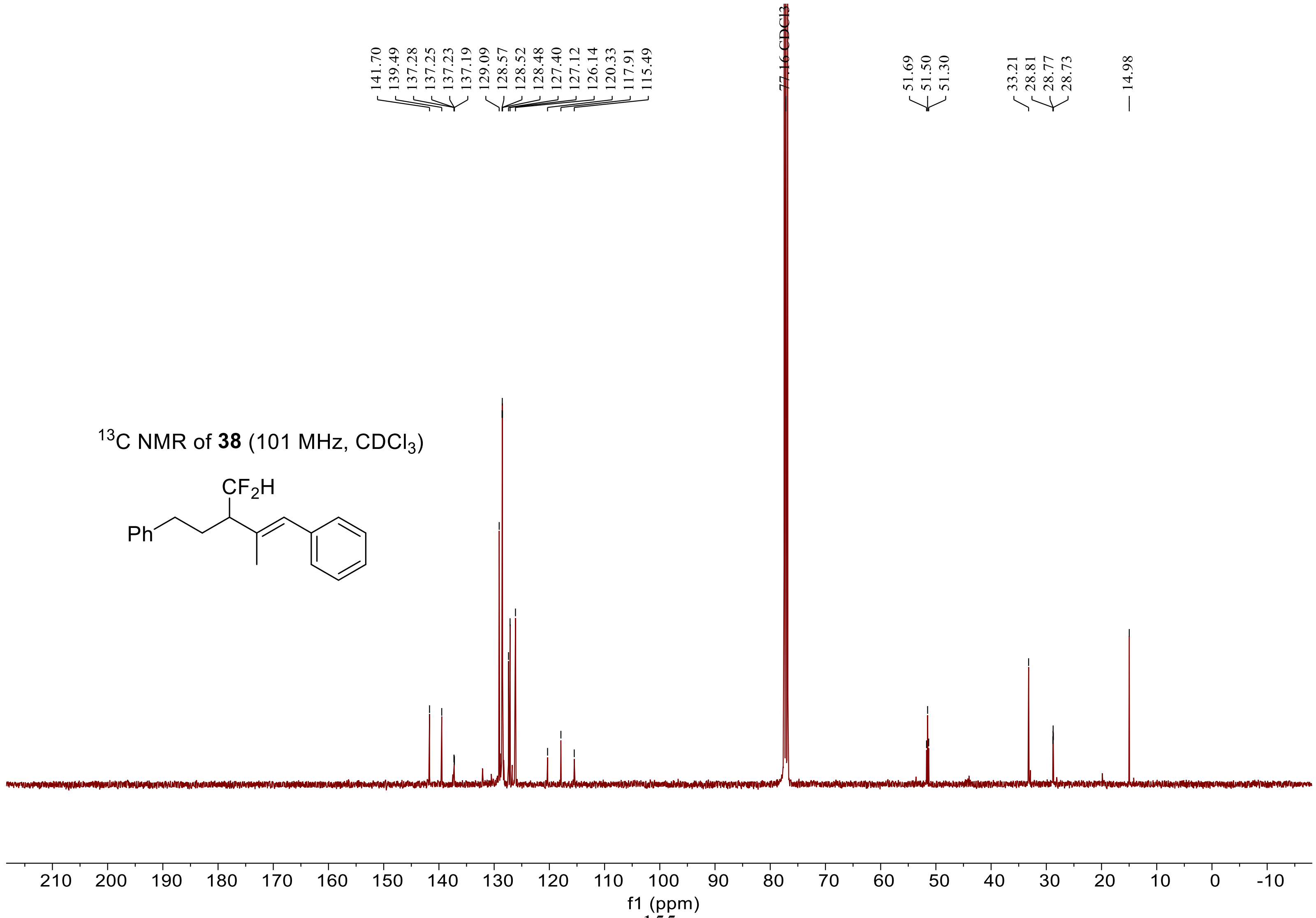

166.82
166.79
144.53
140.93
140.70
139.65
139.63
139.59
131.54
130.32
129.66
129.48
129.30
129.19
128.72
128.50
126.43
119.81
117.38
114.95
77.16 CDCl3
52.38
52.22
52.08
51.88
33.13
29.13
29.10
29.06
^{13}C NMR of **37** (101 MHz, $CDCl_3$)
CF_2H
COOMe
COOMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

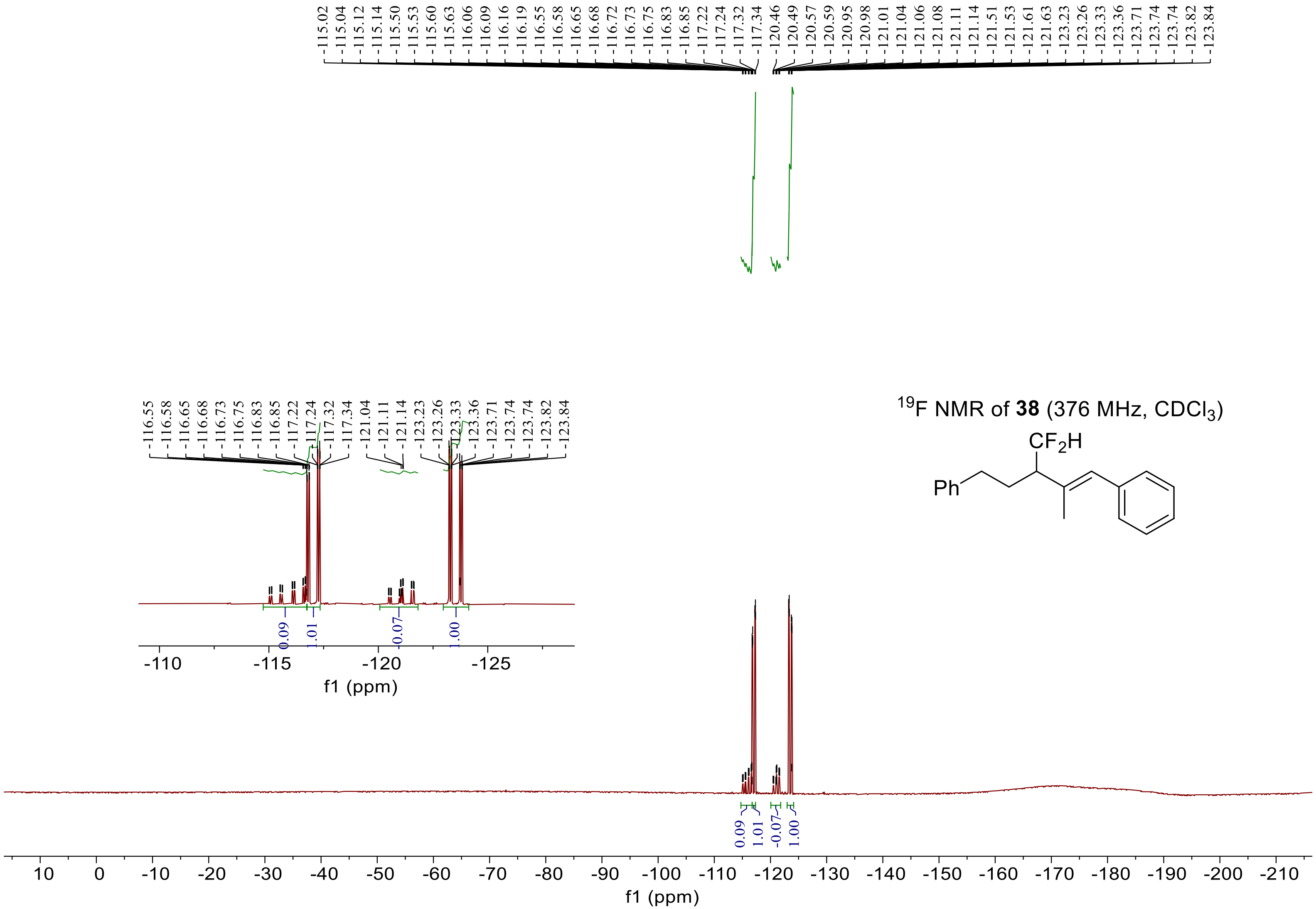


^{19}F NMR of **37** (376 MHz, $CDCl_3$)

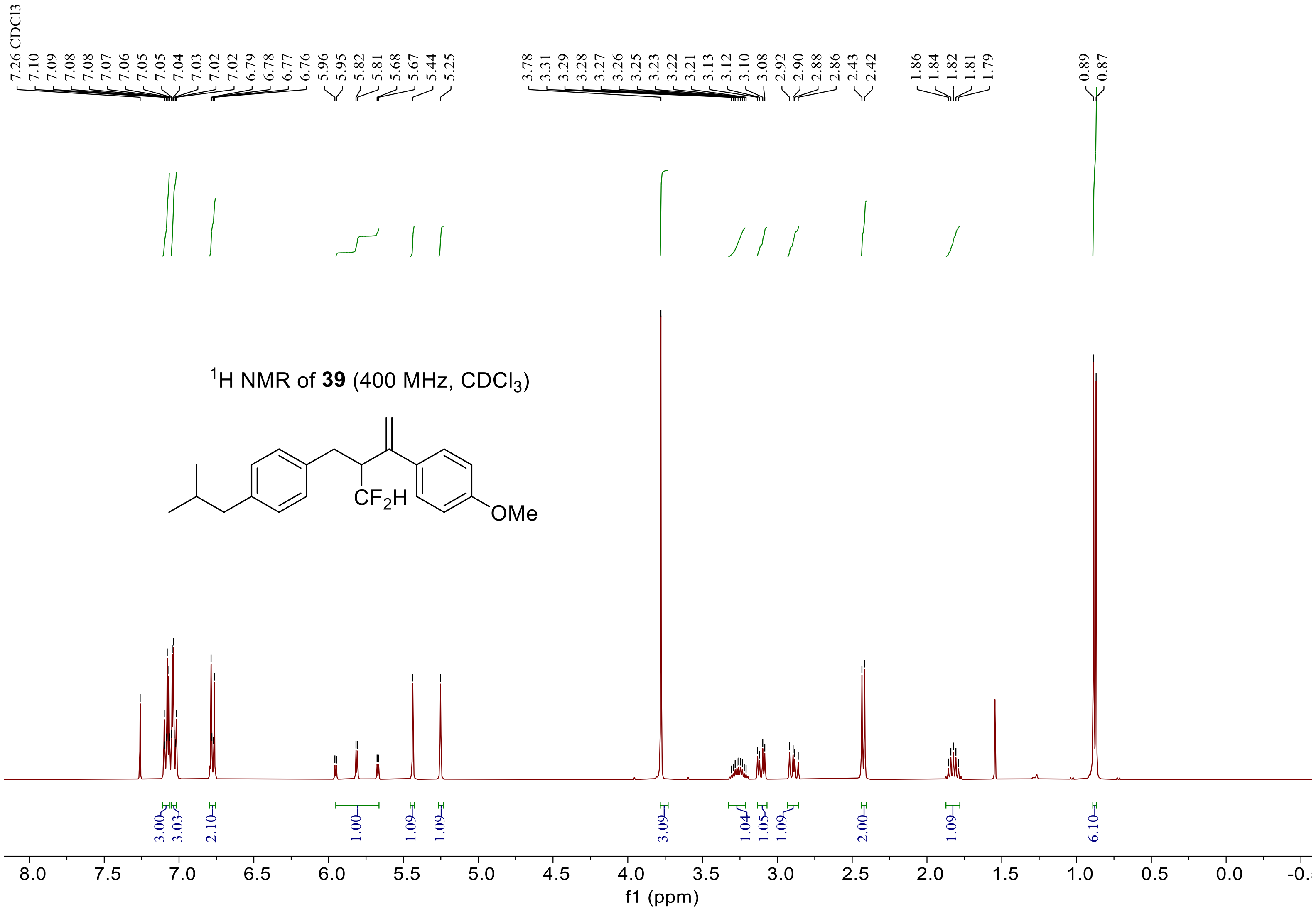
^{1}H NMR of **38** (400 MHz, $CDCl_3$)



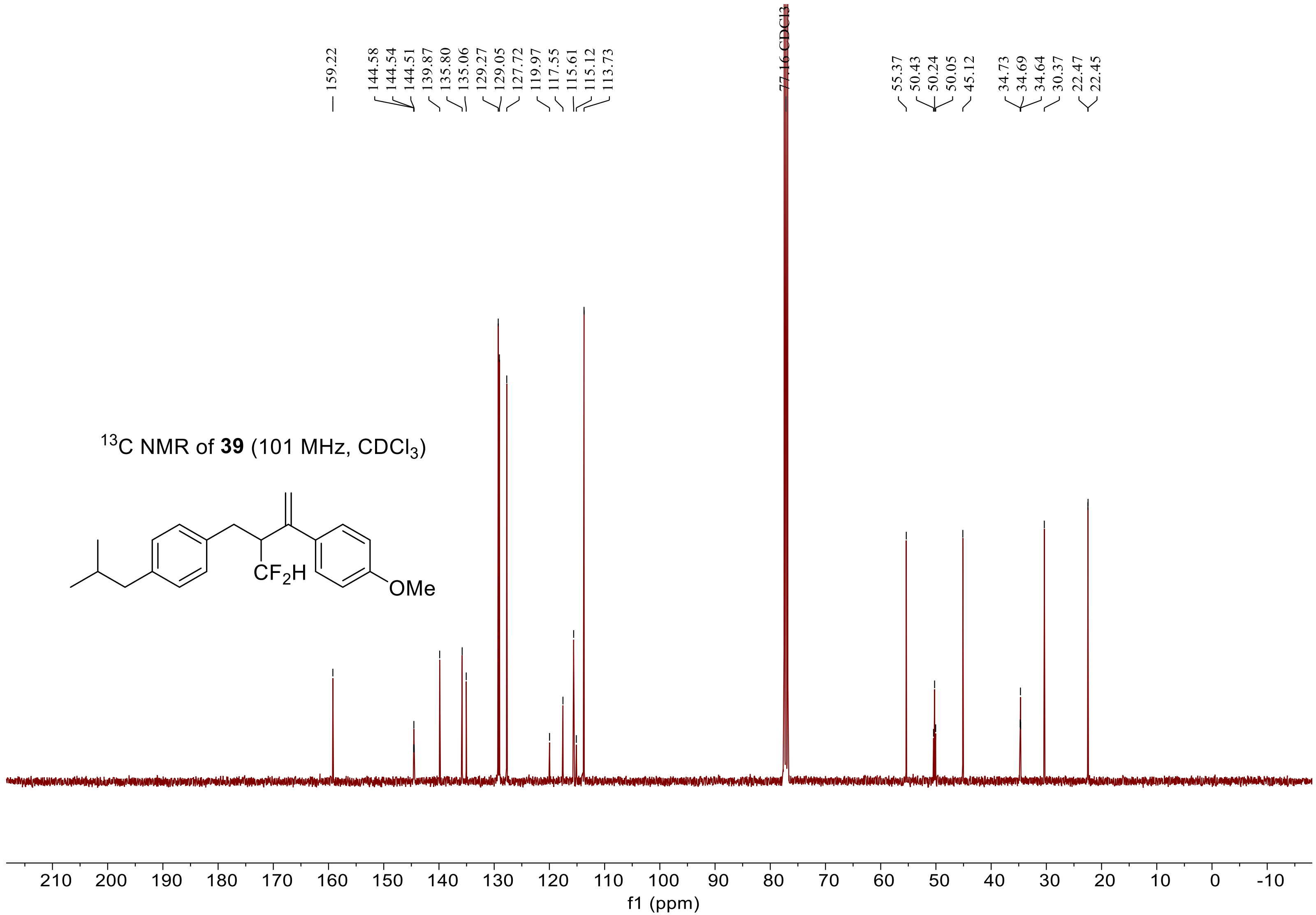

141.70
139.49
137.28
137.25
137.23
137.19
129.09
128.57
128.52
128.48
127.40
127.12
126.14
120.33
117.91
115.49
77.16 CDCl3
51.69
51.50
51.30
33.21
28.81
28.77
28.73
14.98
^{13}C NMR of **38** (101 MHz, $CDCl_3$)
CF_2H
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

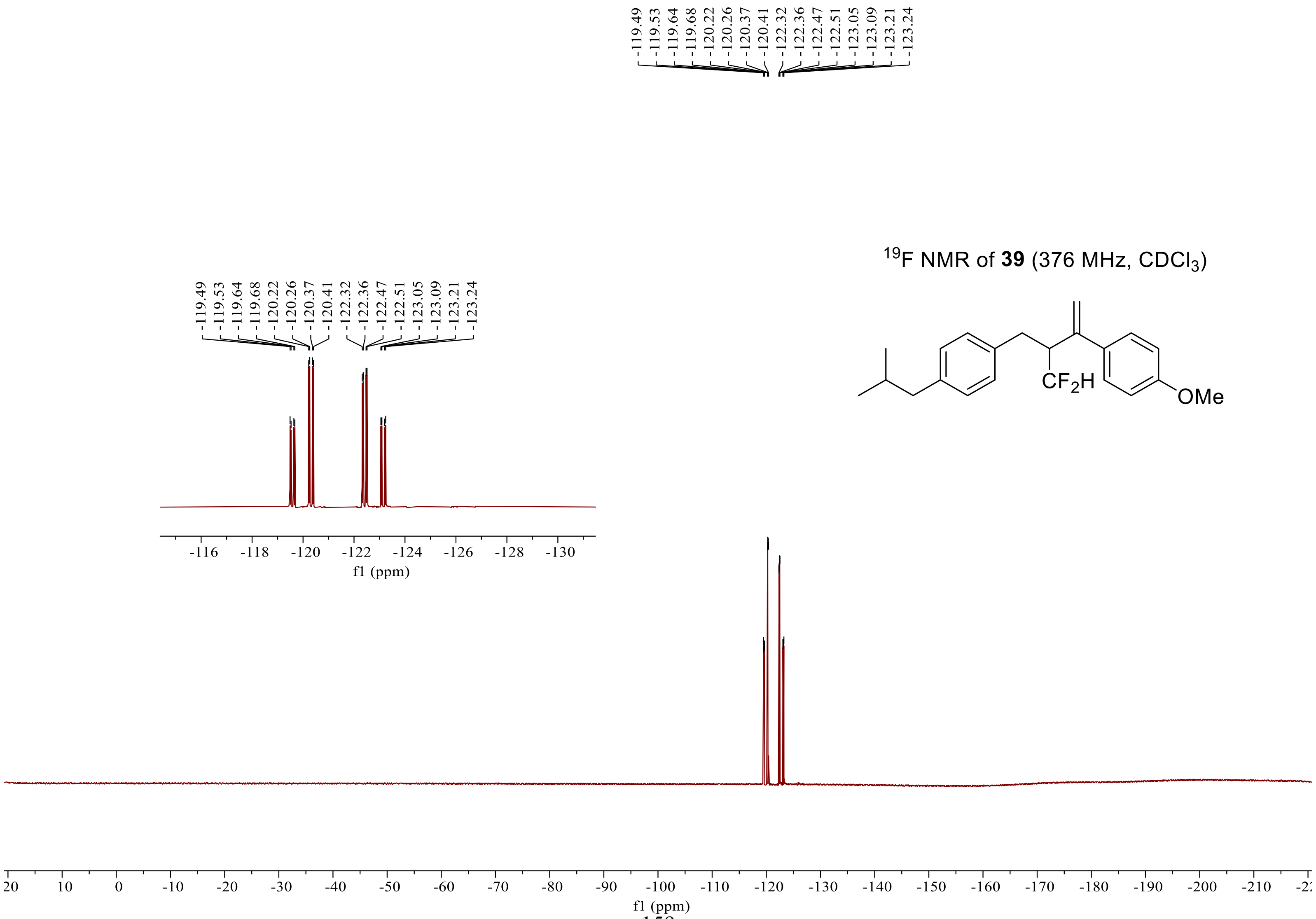


^{19}F NMR of **38** (376 MHz, $CDCl_3$)
CF_2H
Ph
f1 (ppm)

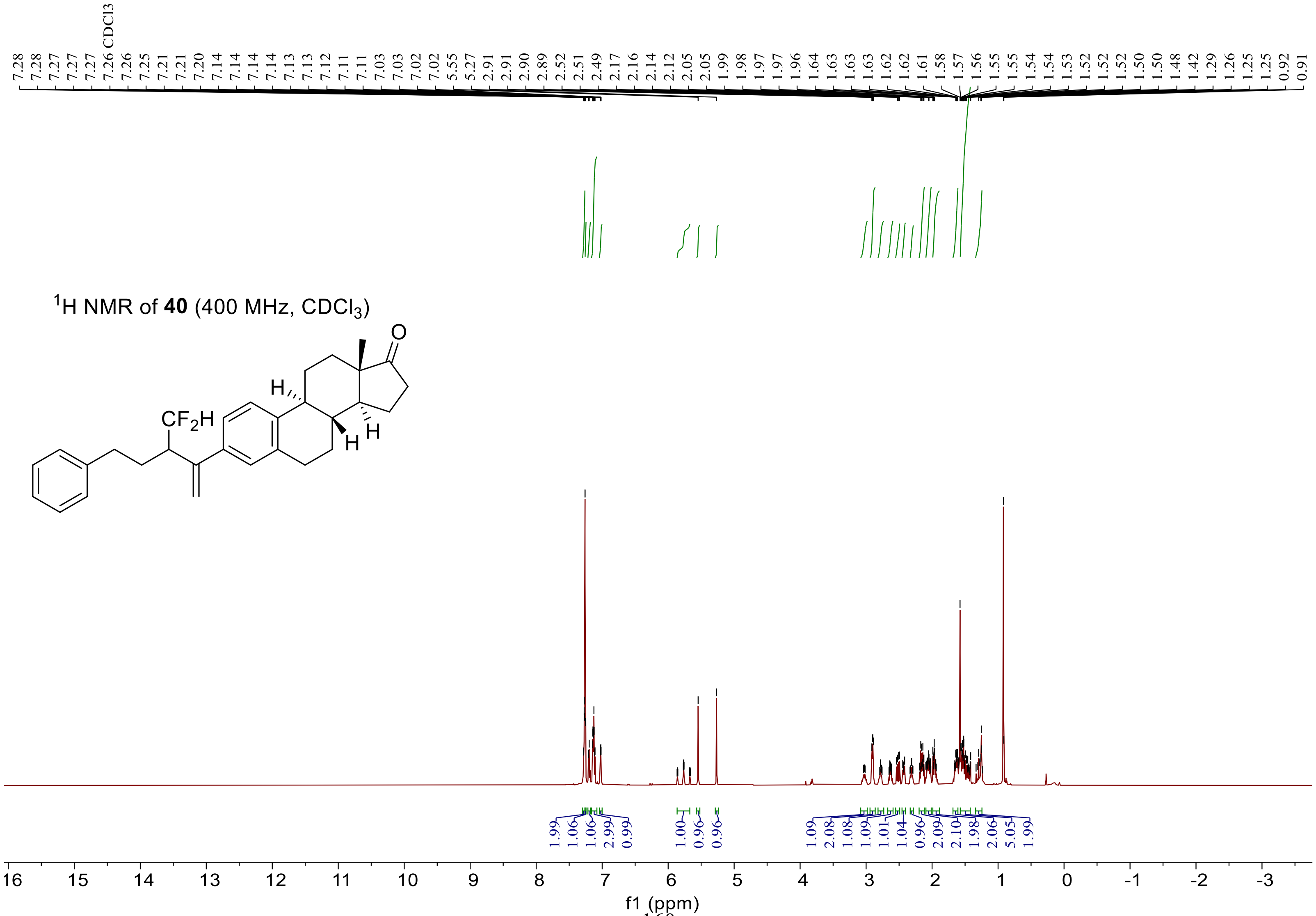


7.26 CDCl3
7.10
7.09
7.08
7.08
7.07
7.06
7.05
7.05
7.04
7.03
7.02
7.02
6.79
6.78
6.77
6.76
5.96
5.95
5.82
5.81
5.68
5.67
5.44
5.25
3.78
3.31
3.29
3.28
3.27
3.26
3.25
3.23
3.22
3.21
3.13
3.12
3.10
3.08
2.92
2.90
2.88
2.86
2.43
2.42
1.86
1.84
1.82
1.81
1.79
0.89
0.87
1H NMR of 39 (400 MHz, CDCl3)
CF2H
OMe
3.00
3.03
2.10
1.00
1.09
1.09
3.09
1.04
1.05
1.09
2.00
1.09
6.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

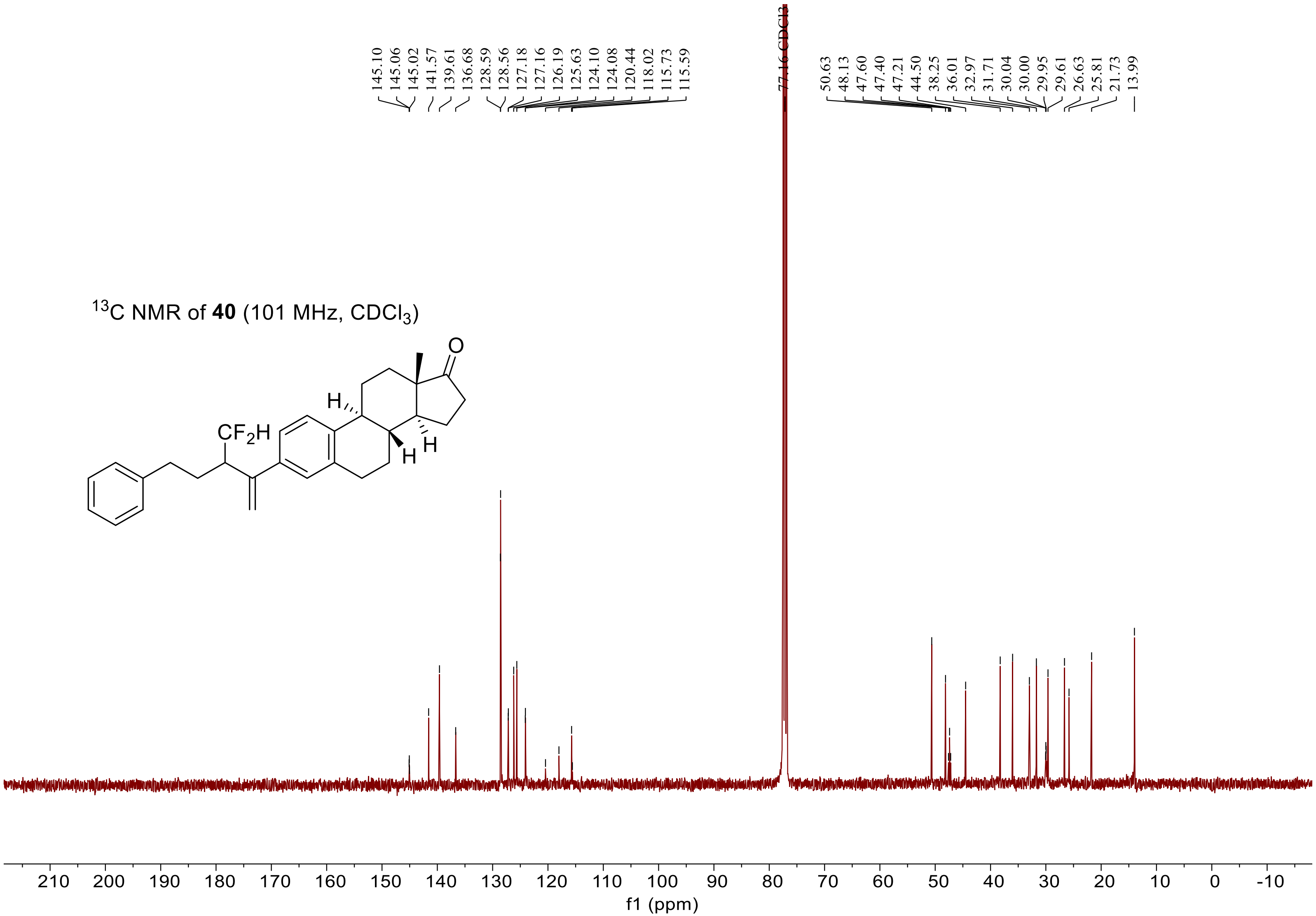

^{13}C NMR of **39** (101 MHz, $CDCl_3$)
CF2H
OMe
159.22
144.58
144.54
144.51
139.87
135.80
135.06
129.27
129.05
127.72
119.97
117.55
115.61
115.12
113.73
77.16 CDCl3
55.37
50.43
50.24
50.05
45.12
34.73
34.69
34.64
30.37
22.47
22.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



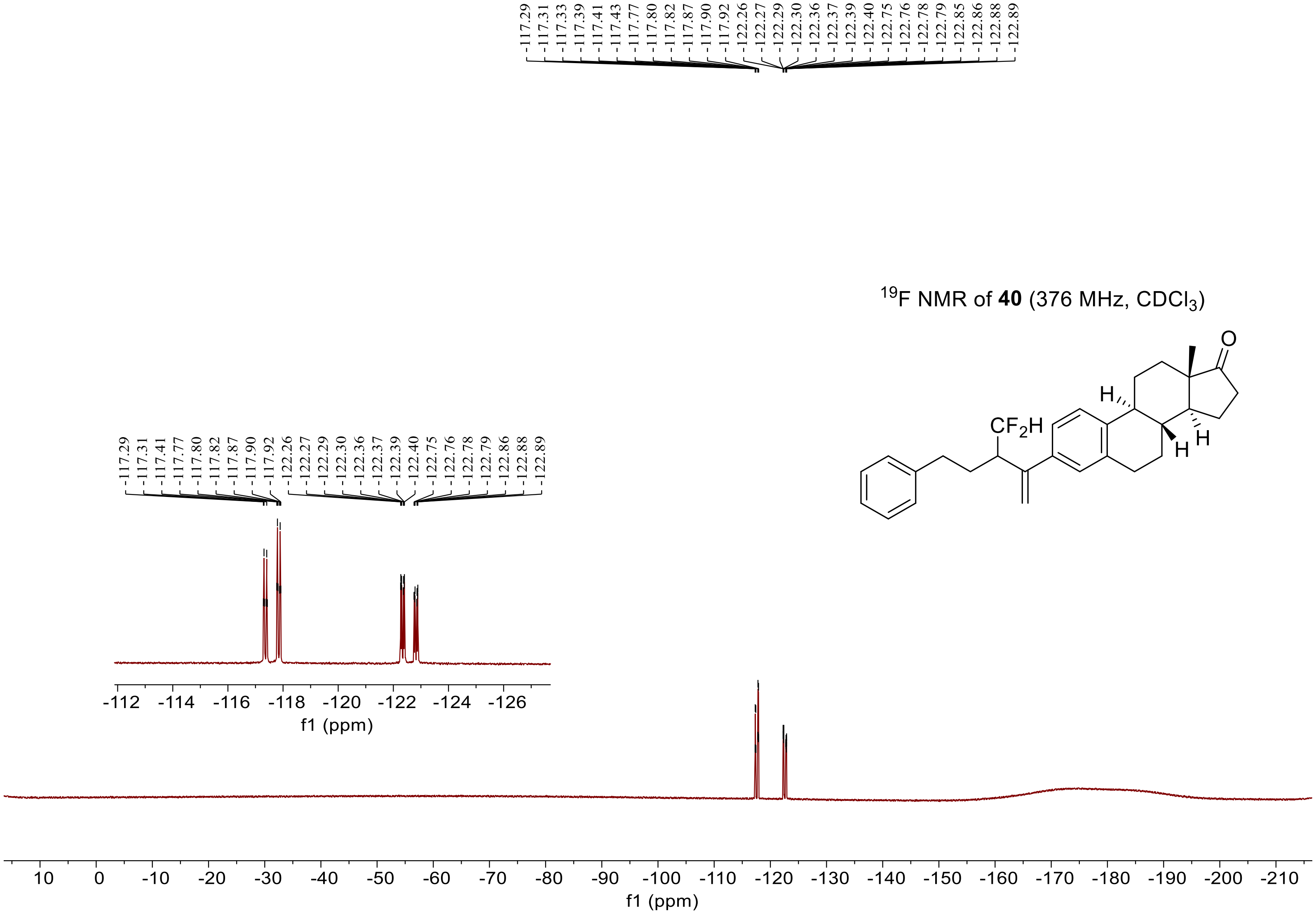
^{19}F NMR of **39** (376 MHz, $CDCl_3$)



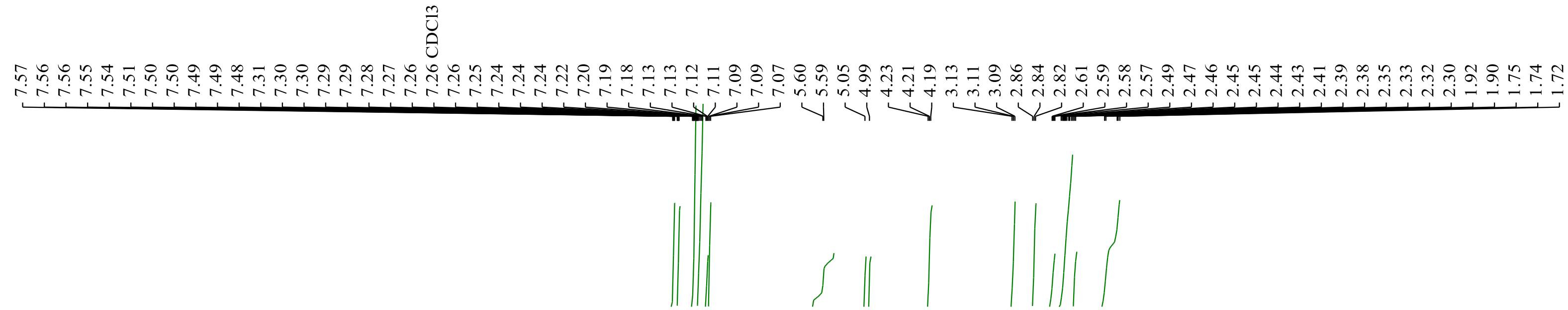
^{1}H NMR of **40** (400 MHz, $CDCl_3$)



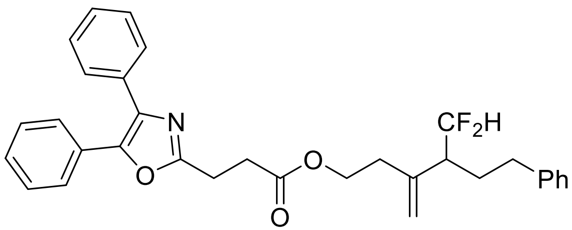
^{13}C NMR of **40** (101 MHz, CDCl$_3$)
145.10
145.06
145.02
141.57
139.61
136.68
128.59
128.56
127.18
127.16
126.19
125.63
124.10
124.08
120.44
118.02
115.73
115.59
77.16 CDCl3
50.63
48.13
47.60
47.40
47.21
44.50
38.25
36.01
32.97
31.71
30.04
30.00
29.95
29.61
26.63
25.81
21.73
13.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

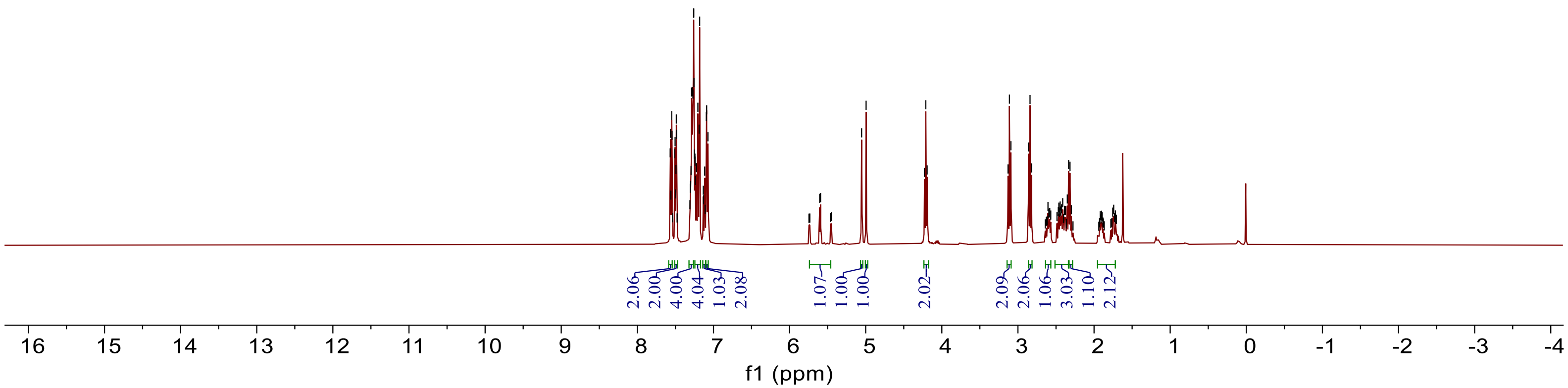


^{19}F NMR of **40** (376 MHz, $CDCl_3$)



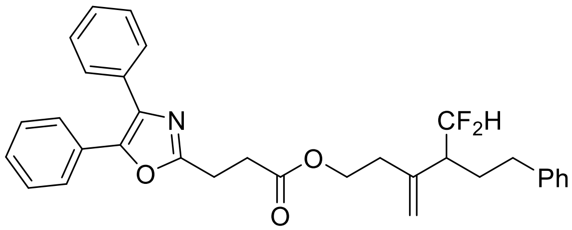
^{1}H NMR of **41** (400 MHz, $CDCl_3$)

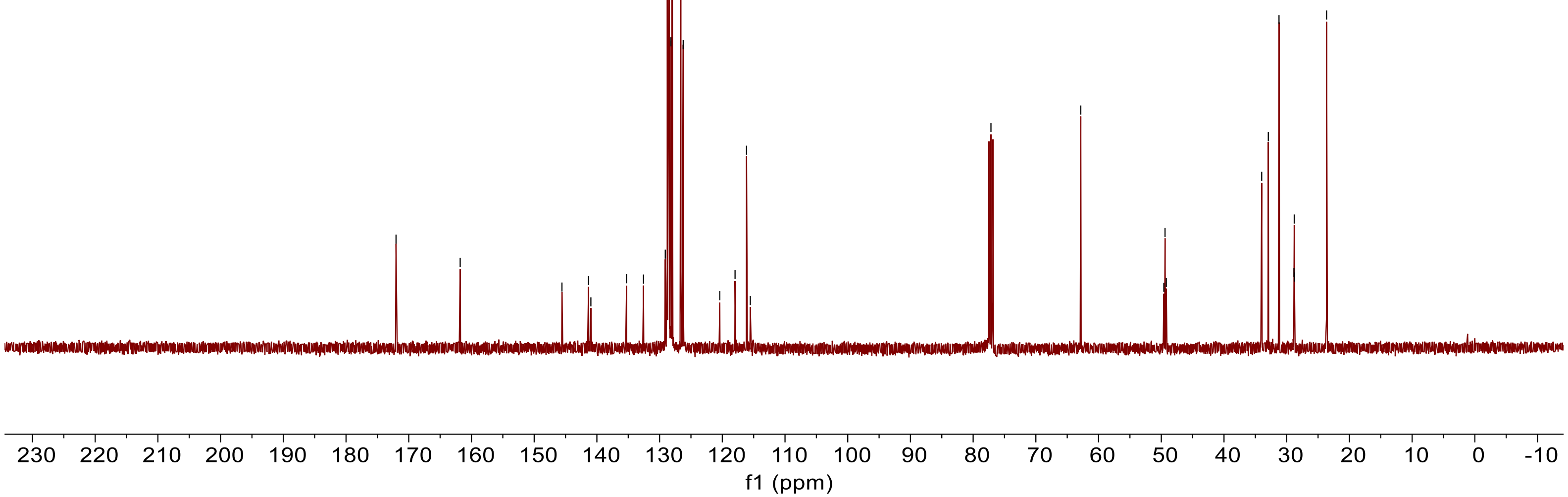




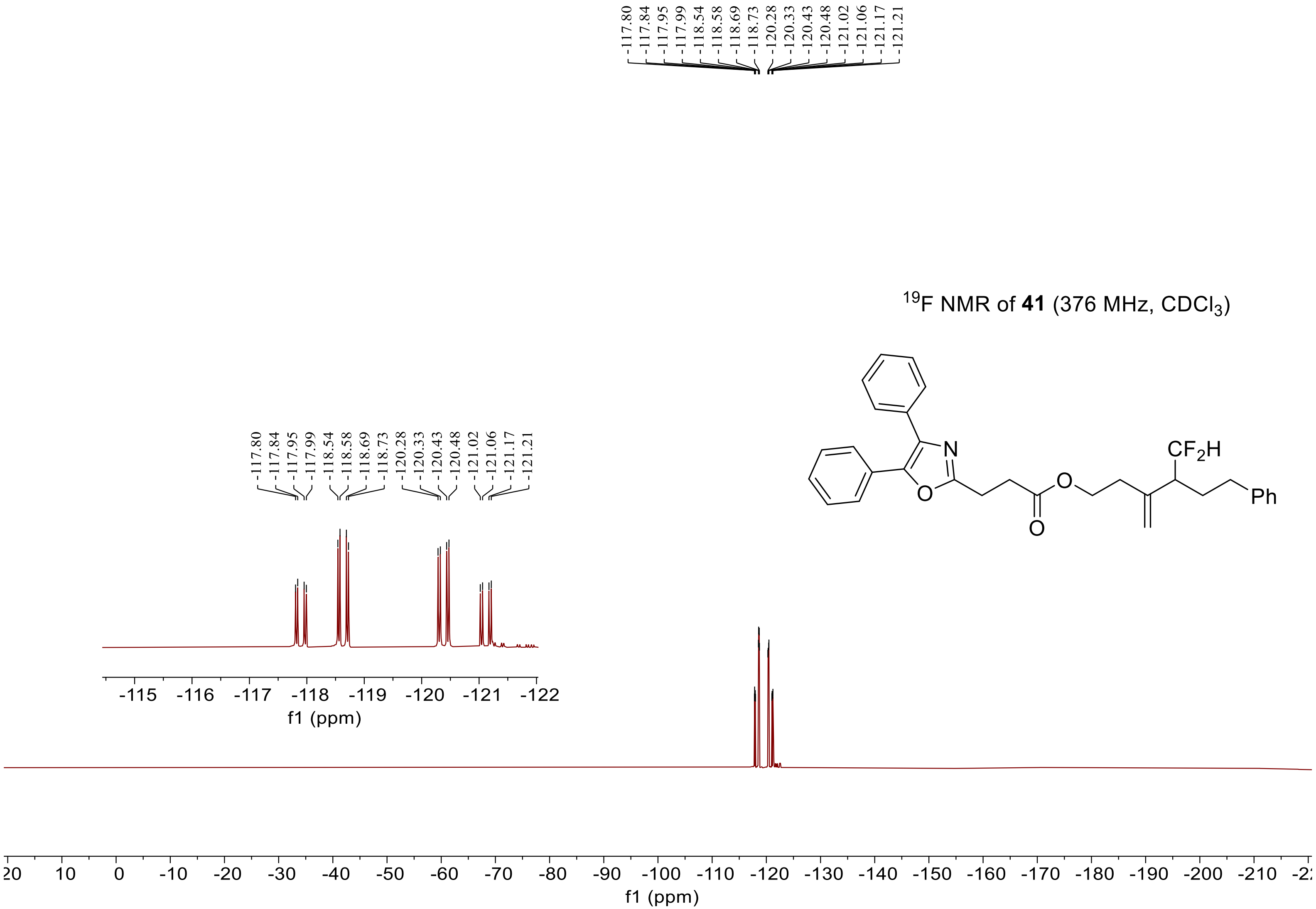
172.03
161.80
145.57
141.33
140.96
135.27
132.57
129.10
128.78
128.68
128.61
128.60
128.47
128.20
128.02
126.61
126.24
120.40
117.97
116.13
115.54
77.16 CDCl3
62.84
49.59
49.40
49.21
33.99
32.94
31.23
28.84
28.80
28.76
23.64

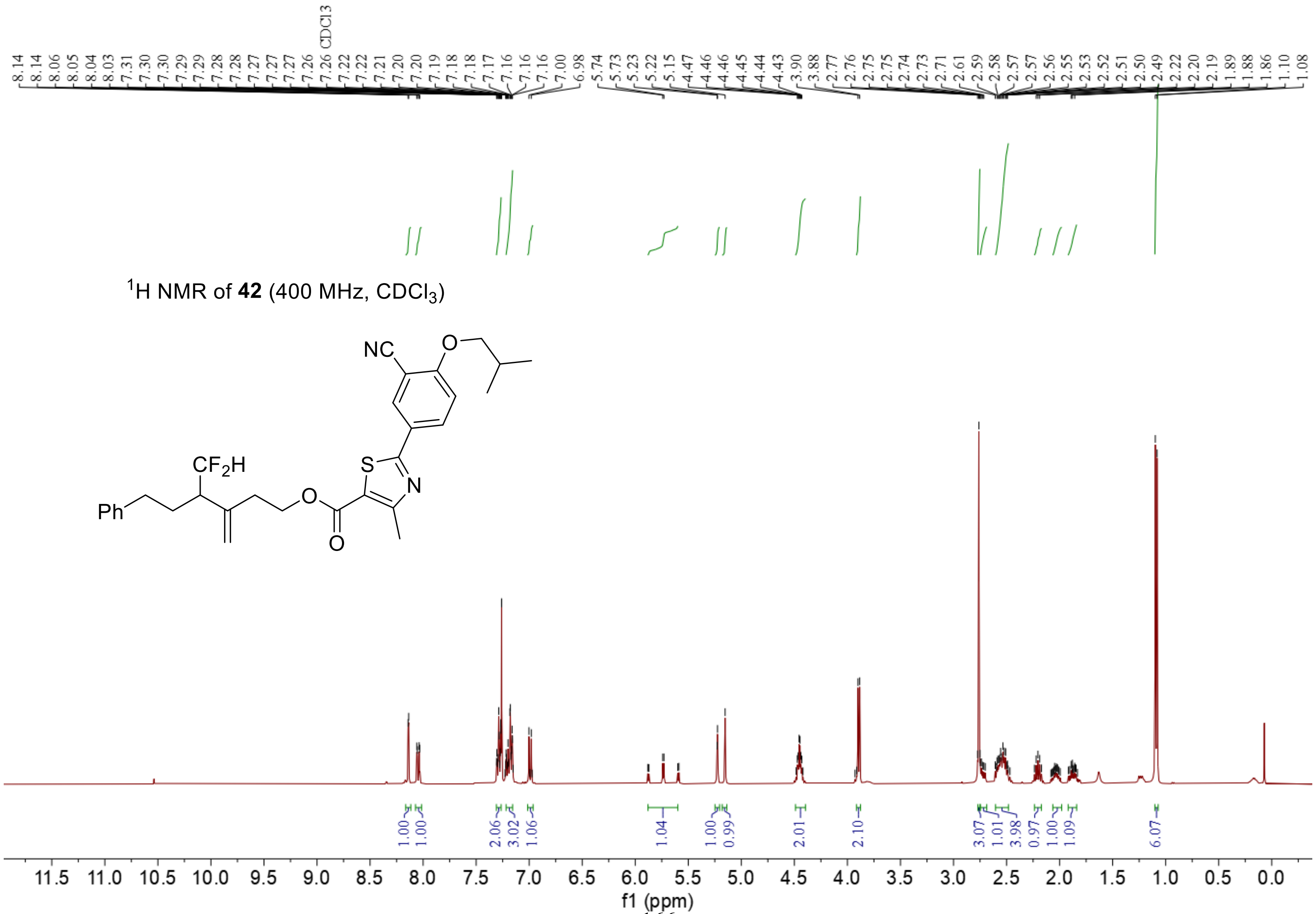
^{13}C NMR of **41** (101 MHz, $CDCl_3$)





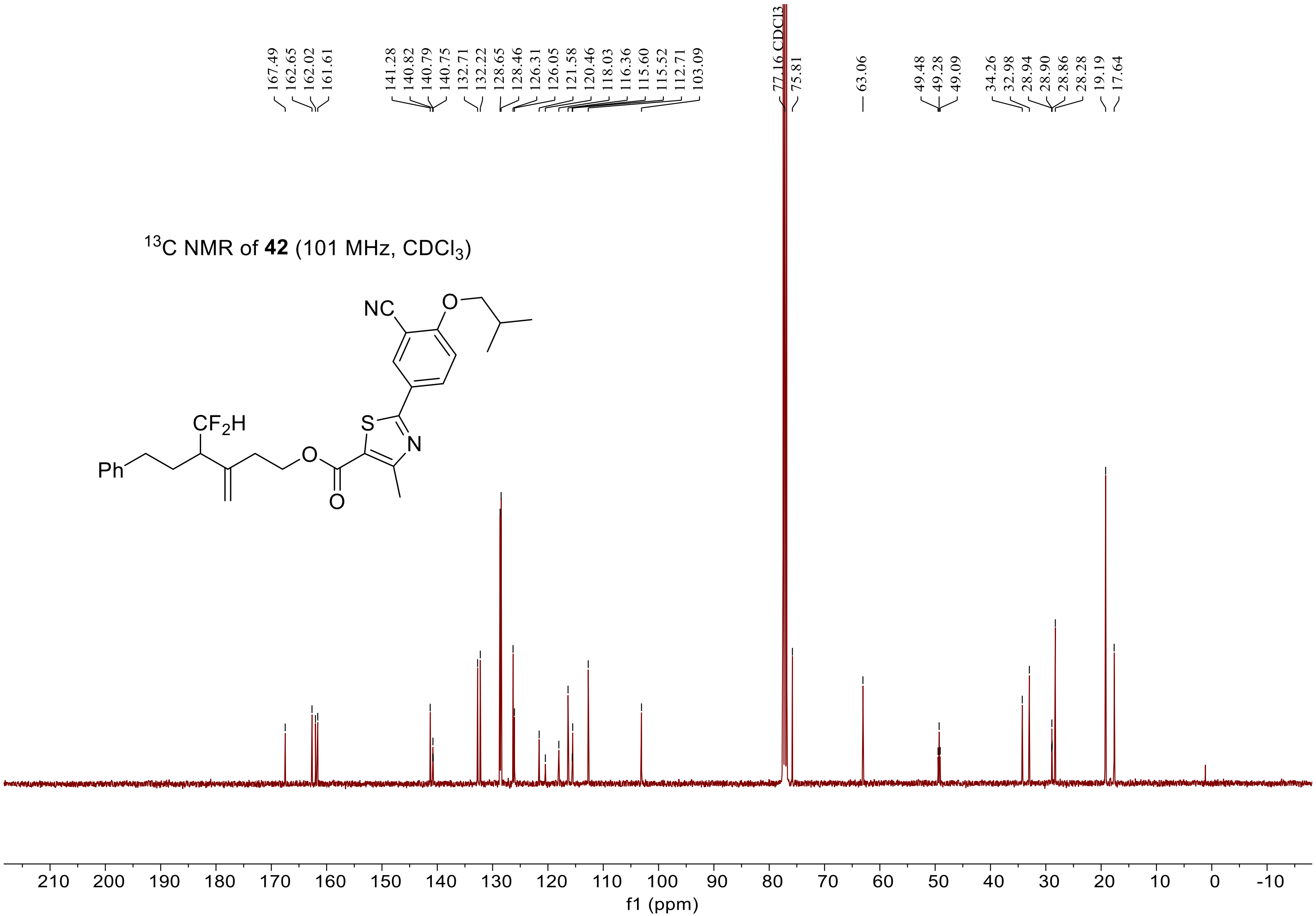
^{19}F NMR of **41** (376 MHz, $CDCl_3$)

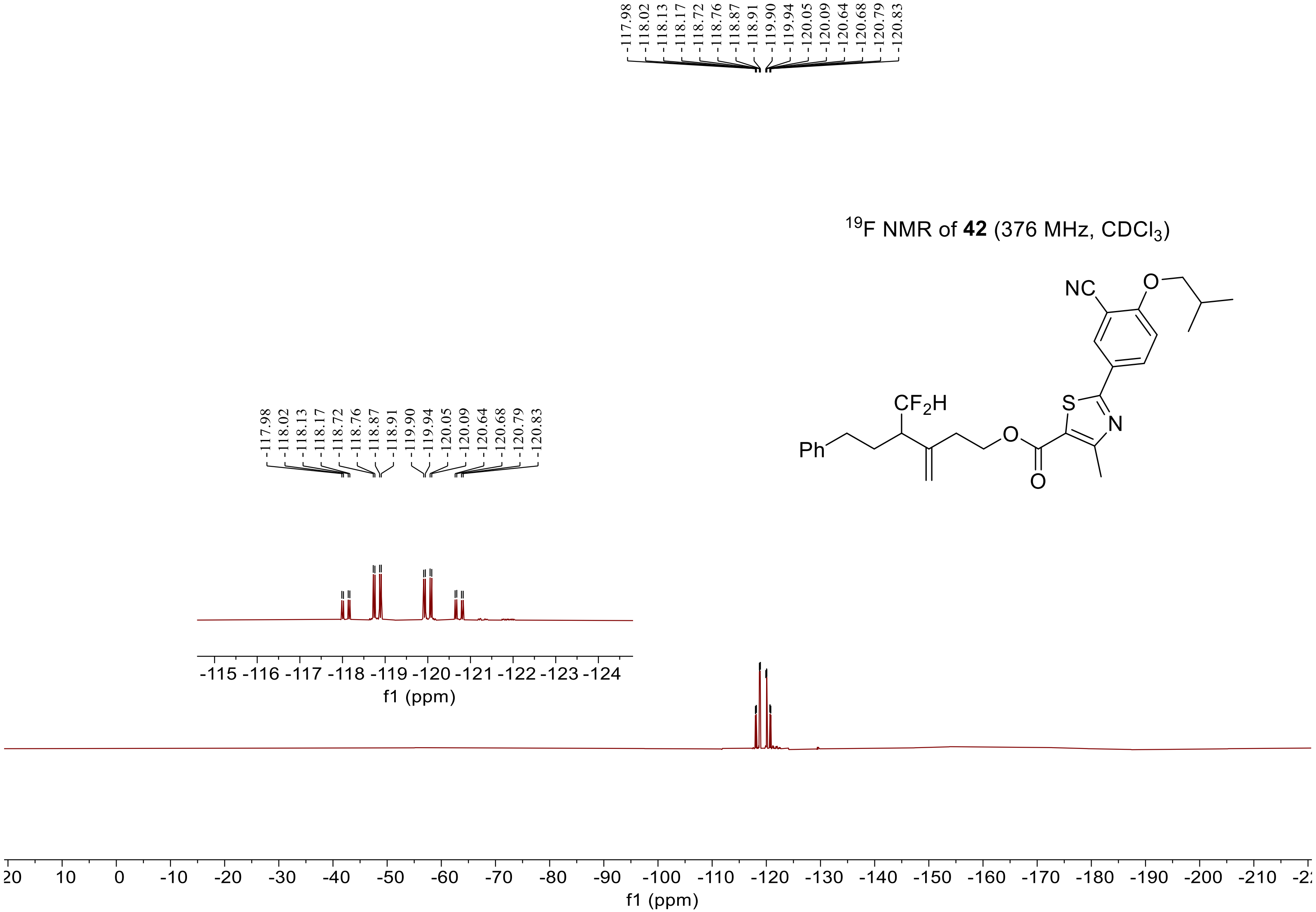




[1]H NMR of **42** (400 MHz, $CDCl_3$)

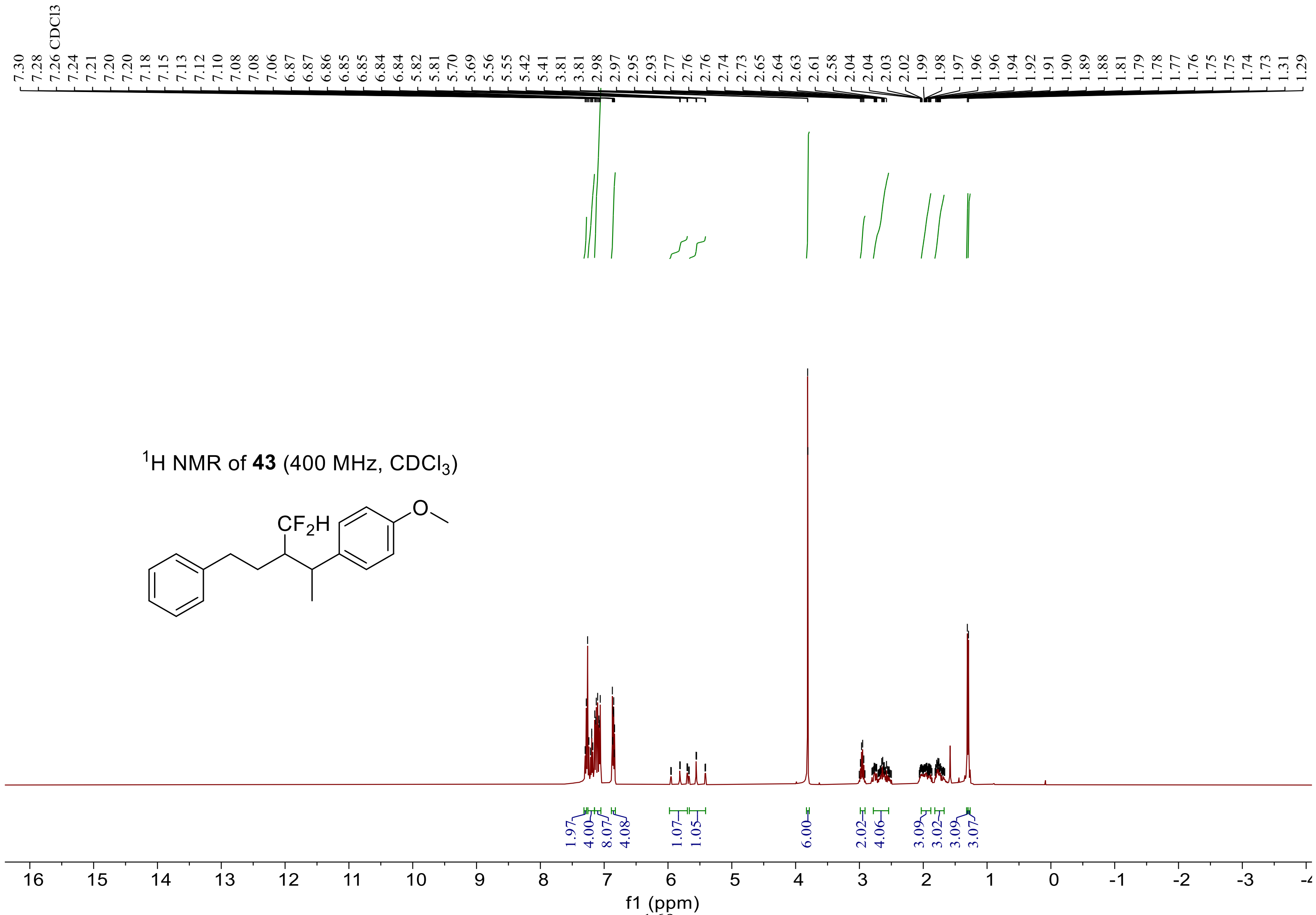
^{13}C NMR of **42** (101 MHz, $CDCl_3$)

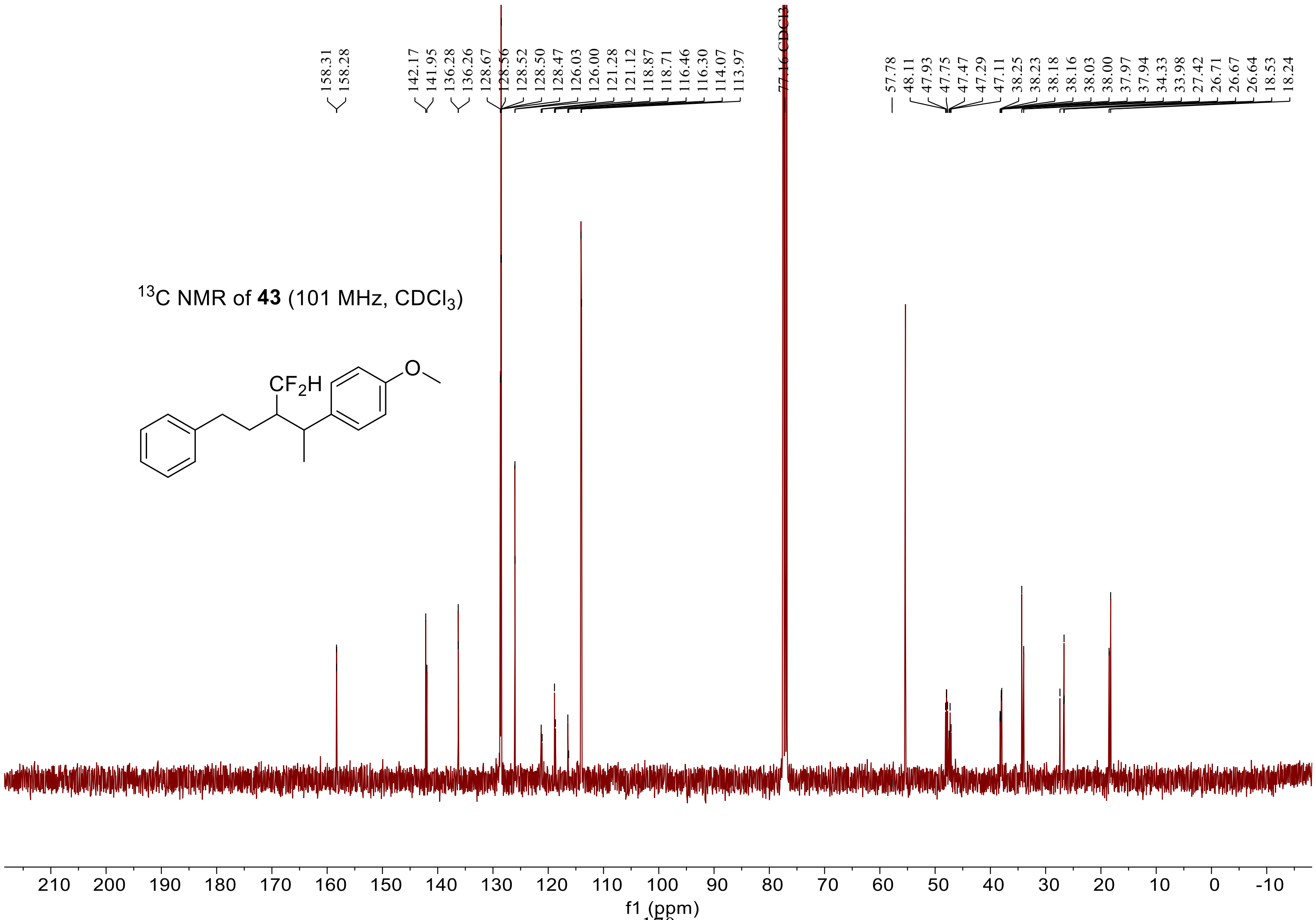




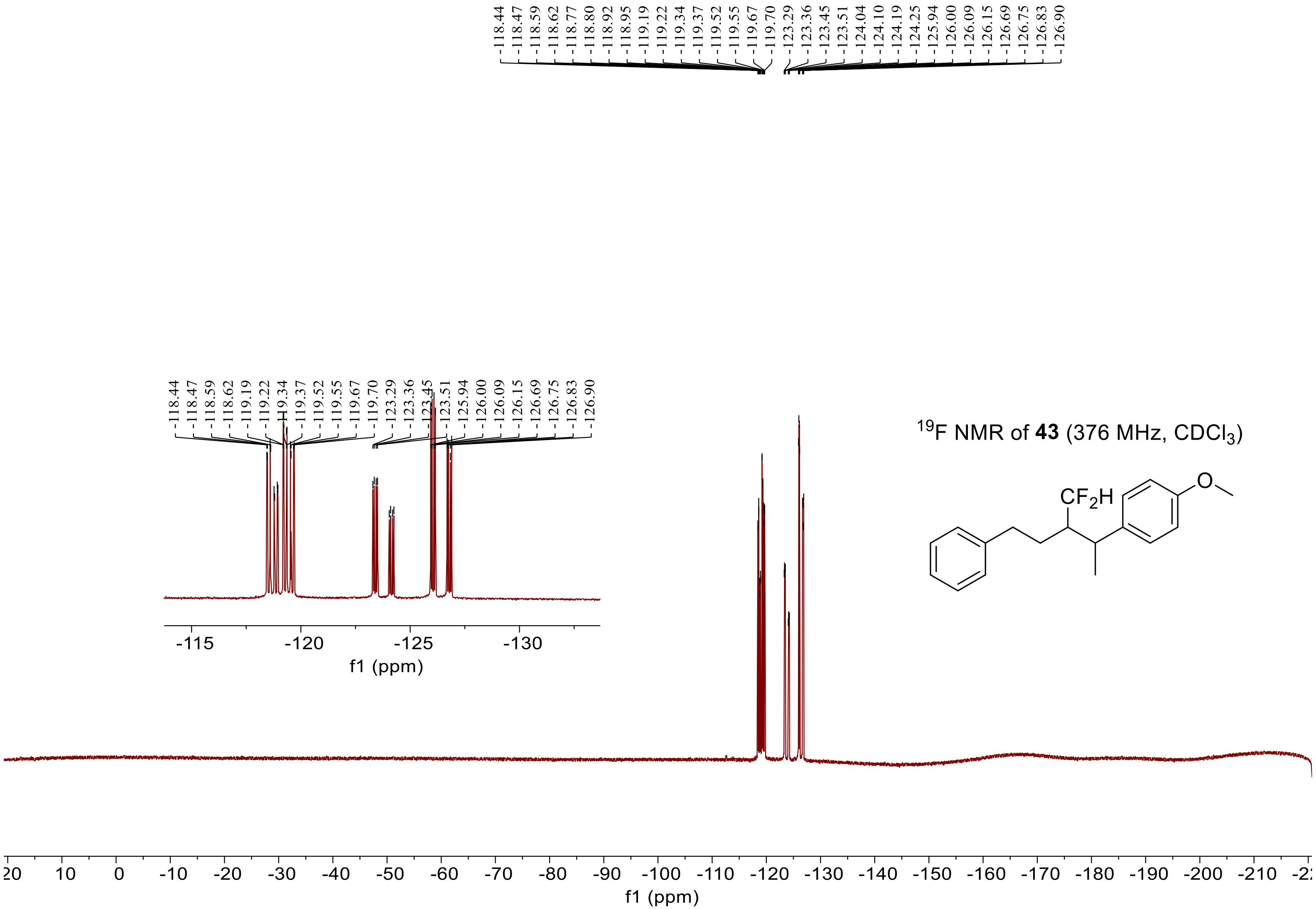
^{19}F NMR of **42** (376 MHz, $CDCl_3$)

[1]H NMR of **43** (400 MHz, $CDCl_3$)

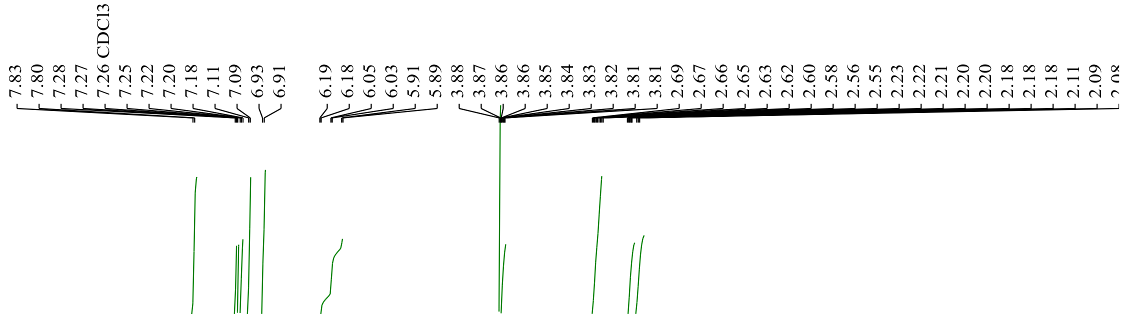




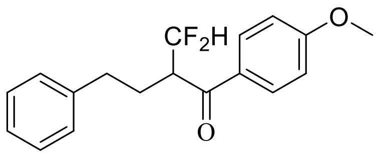
158.31
158.28
142.17
141.95
136.28
136.26
128.67
128.56
128.52
128.50
128.47
126.03
126.00
121.28
121.12
118.87
118.71
116.46
116.30
114.07
113.97
77.16 CDCl3
57.78
48.11
47.93
47.75
47.47
47.29
47.11
38.25
38.23
38.18
38.16
38.03
38.00
37.97
37.94
34.33
33.98
27.42
26.71
26.67
26.64
18.53
18.24
^{13}C NMR of **43** (101 MHz, $CDCl_3$)
CF_2H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

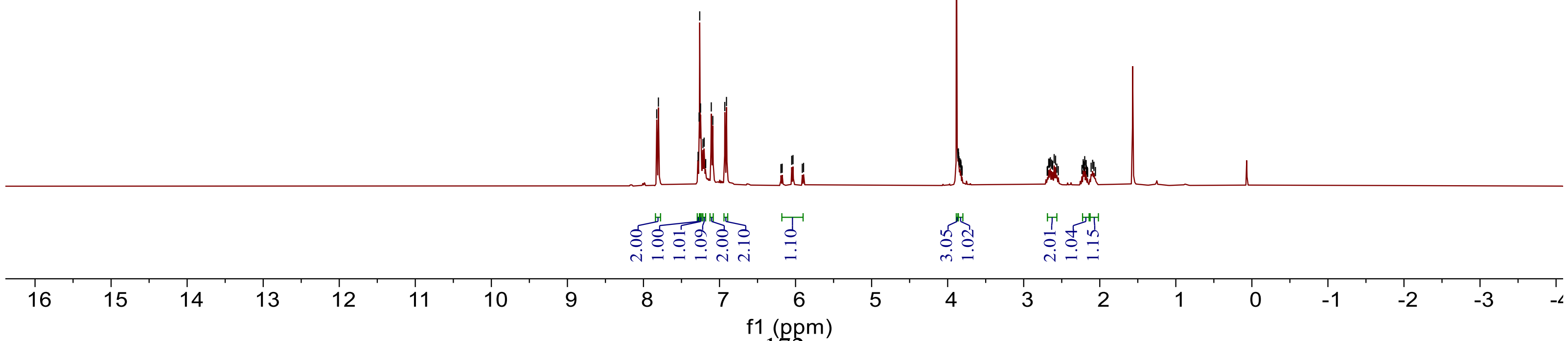


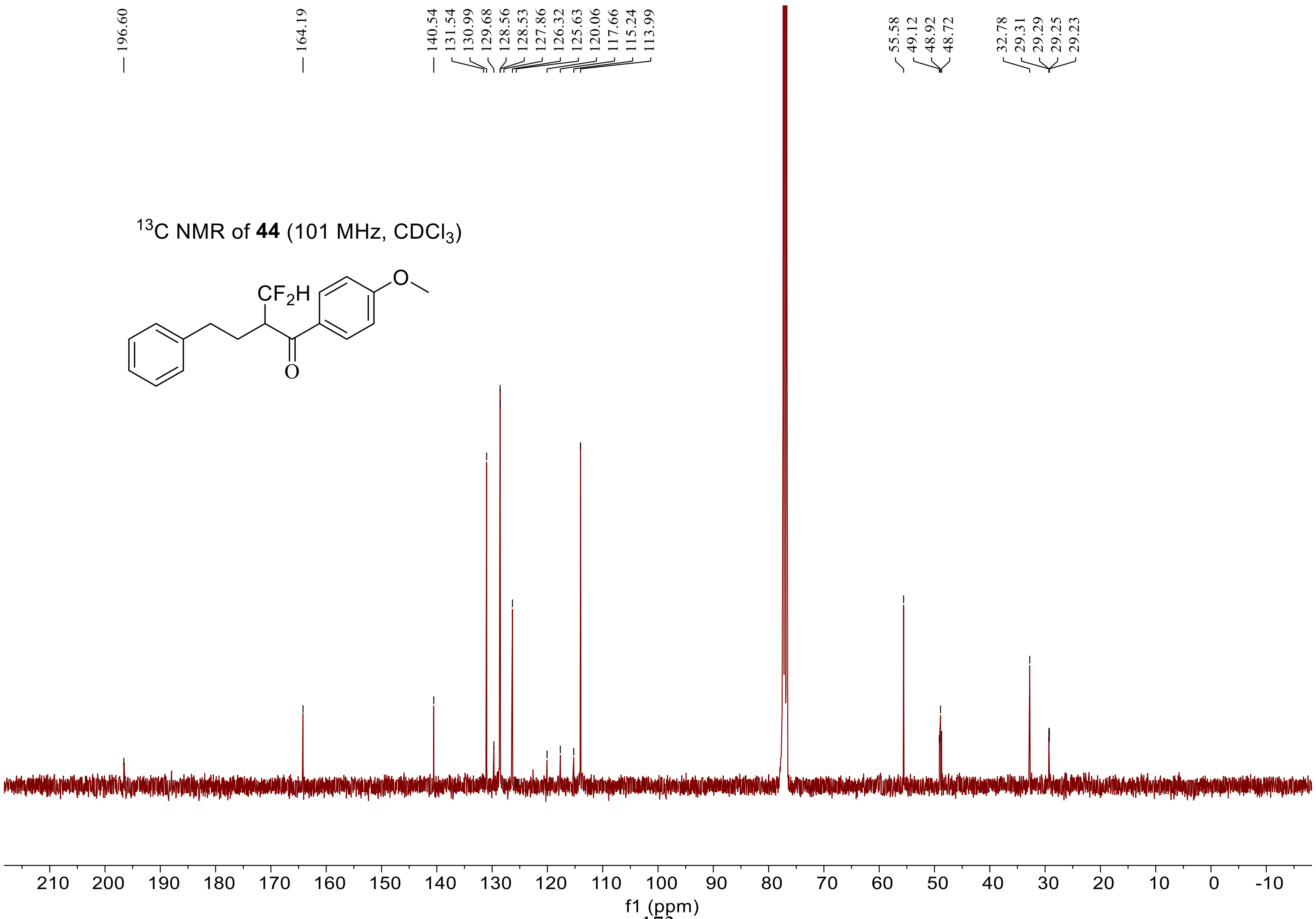
^{19}F NMR of **43** (376 MHz, $CDCl_3$)



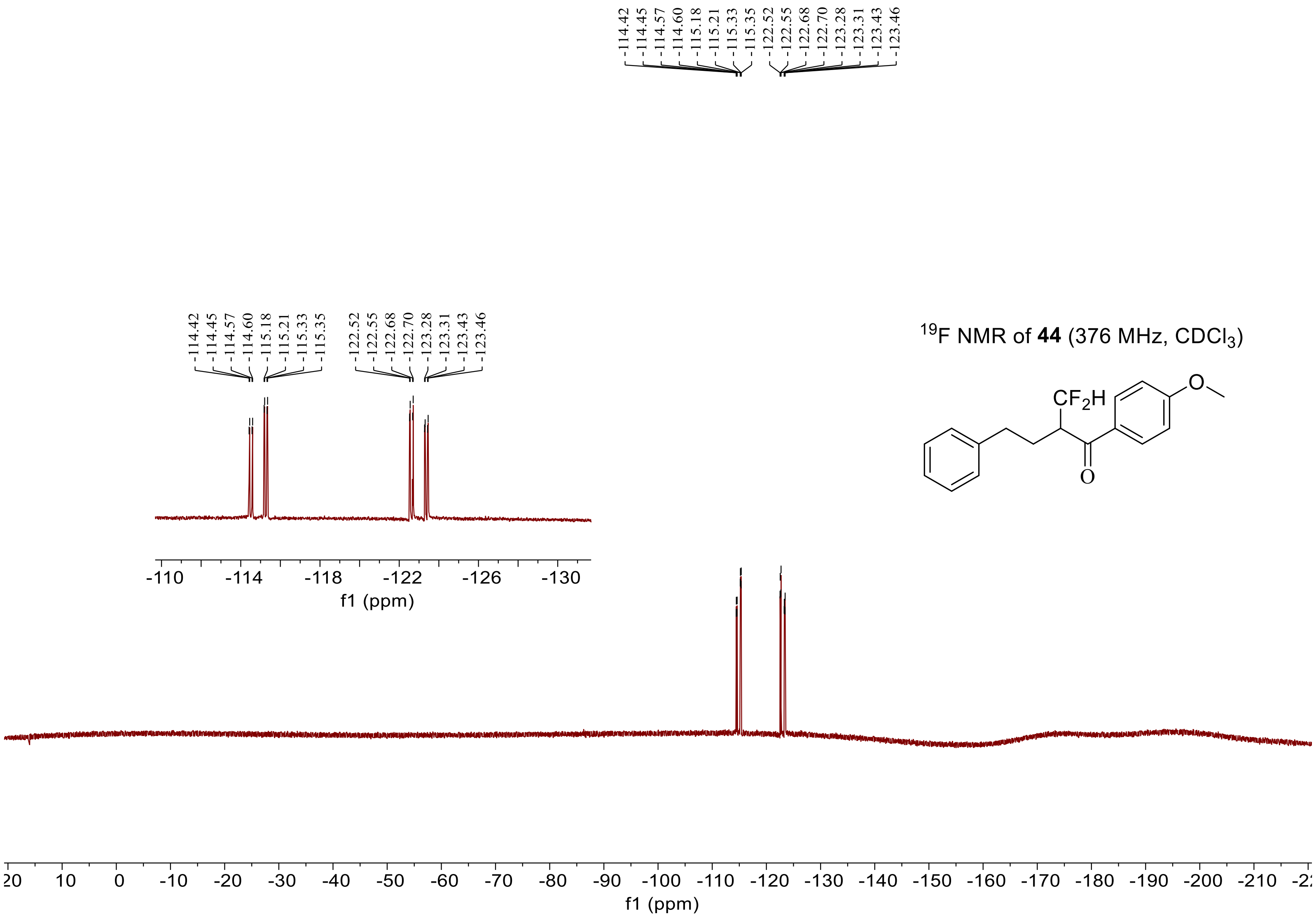
^{1}H NMR of **44** (400 MHz, $CDCl_3$)





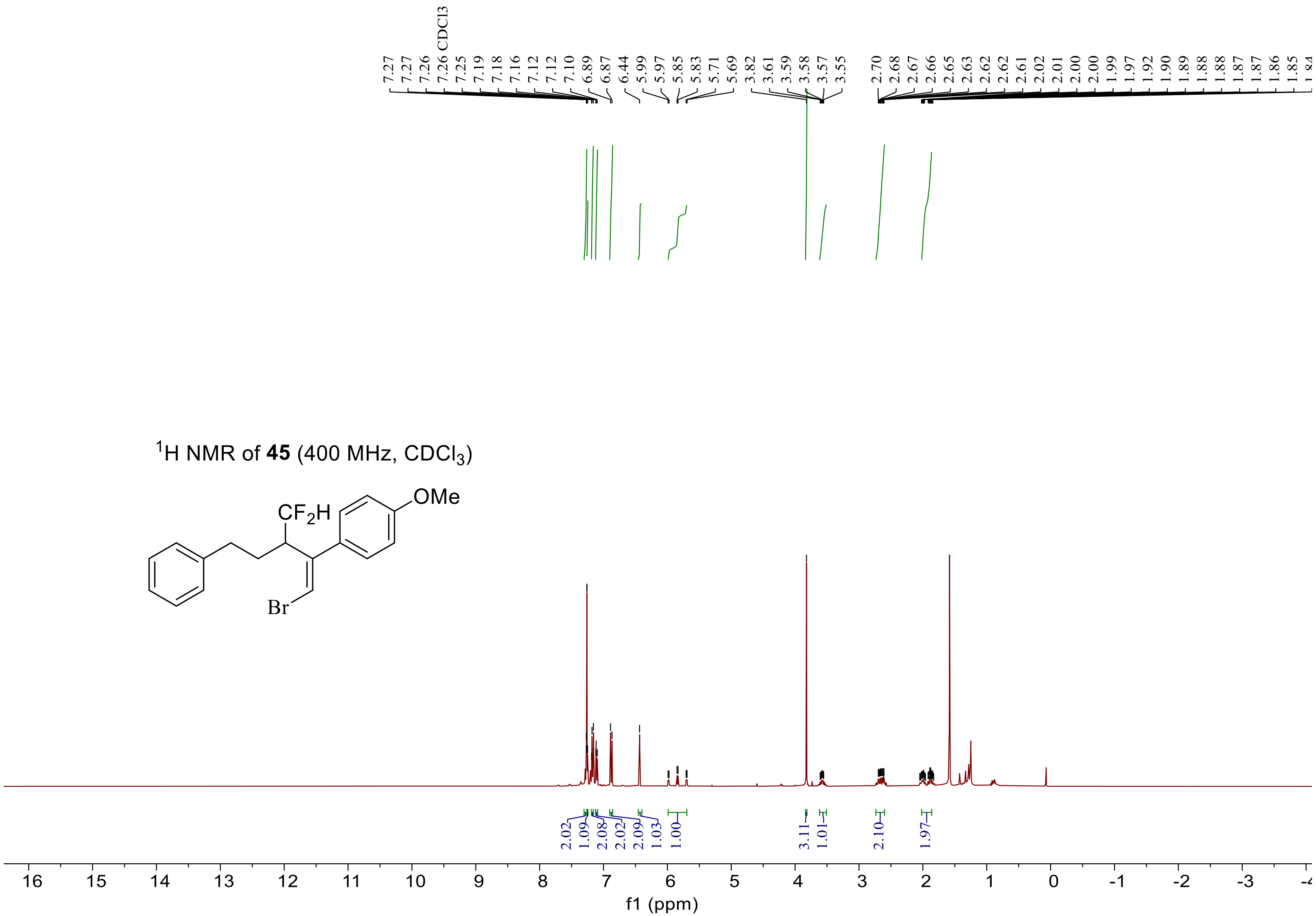


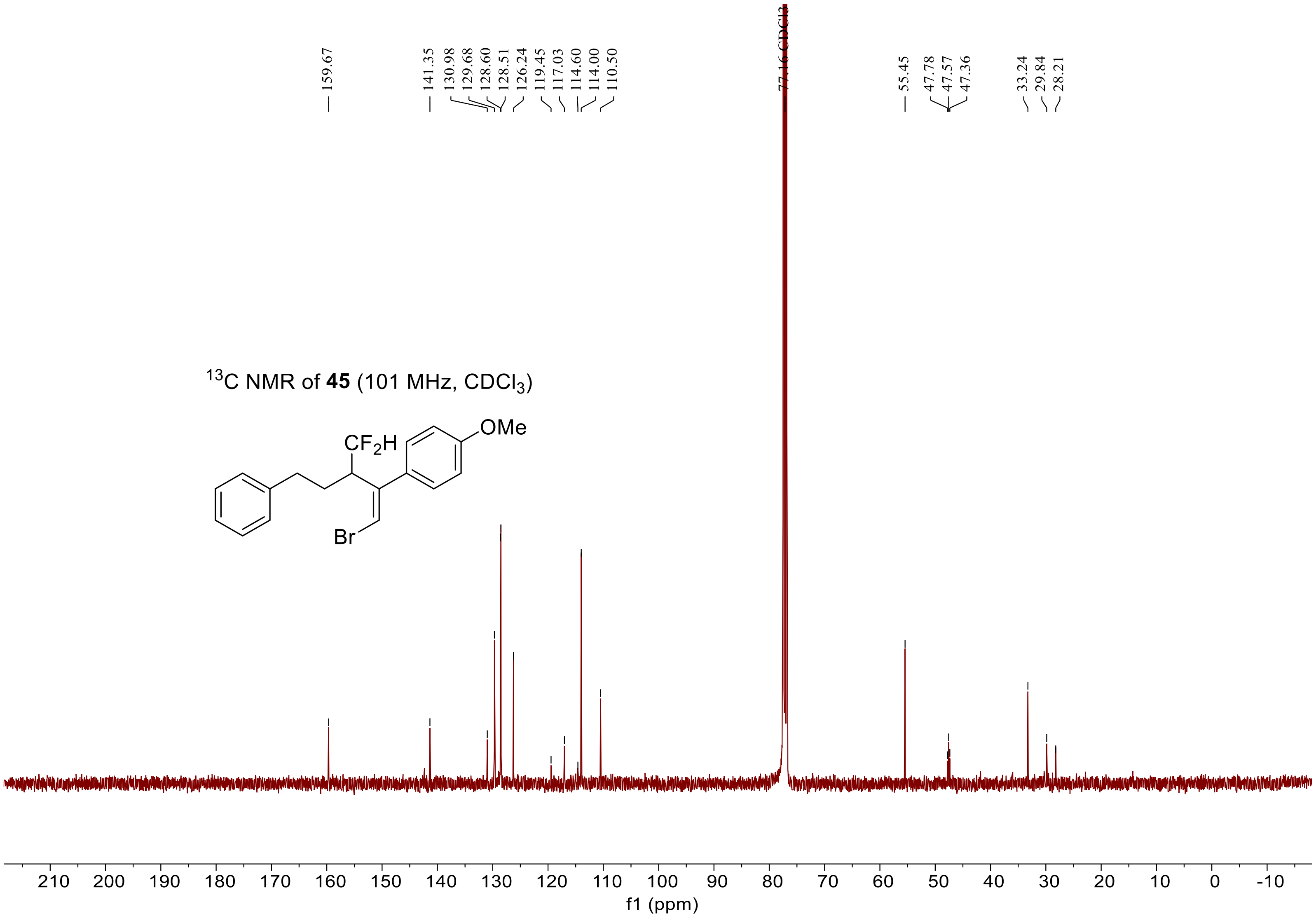
^{13}C NMR of **44** (101 MHz, $CDCl_3$)



^{19}F NMR of **44** (376 MHz, $CDCl_3$)

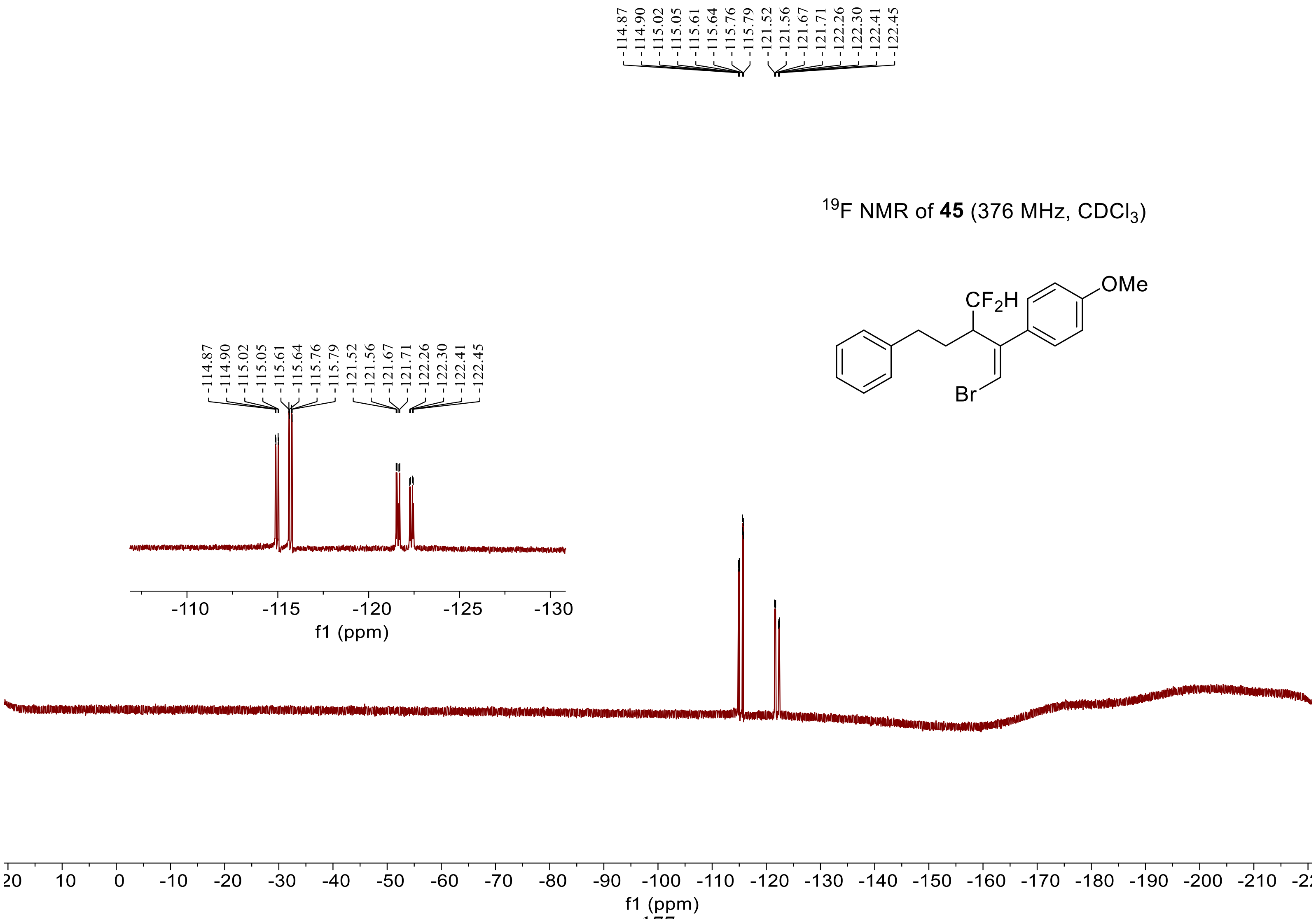
^{1}H NMR of **45** (400 MHz, $CDCl_3$)

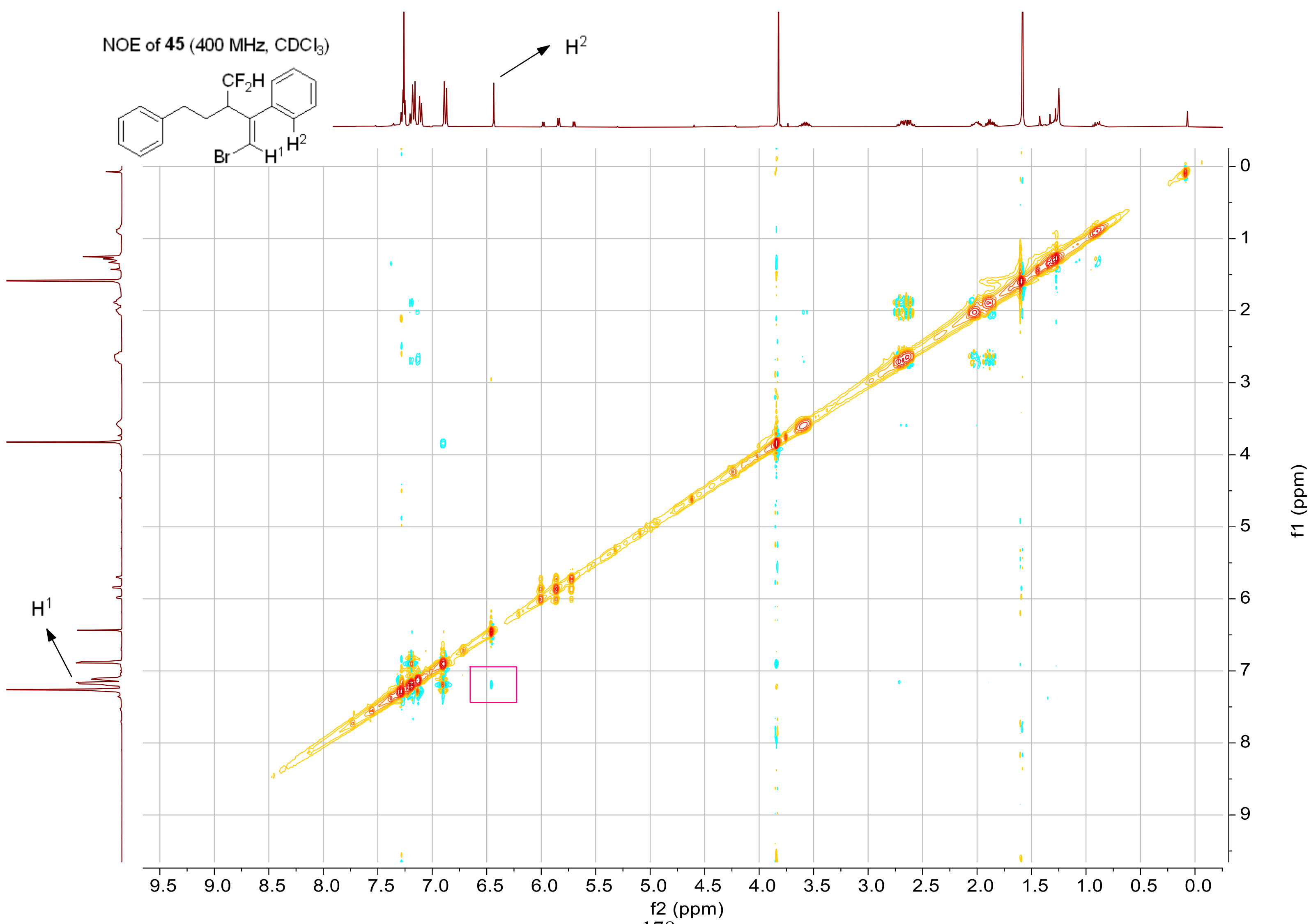




159.67
141.35
130.98
129.68
128.60
128.51
126.24
119.45
117.03
114.60
114.00
110.50
77.16 CDCl3
55.45
47.78
47.57
47.36
33.24
29.84
28.21
13C NMR of 45 (101 MHz, CDCl3)
OMe
CF2H
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR of **45** (376 MHz, $CDCl_3$)




NOE of 45 (400 MHz, CDCl3)
CF2H
Br
H1
H2
f2 (ppm)
f1 (ppm)